1974

# Nonconducting pores in soils.

Olaf Lee Weeks
*University of Massachusetts Amherst*

# NONCONDUCTING PORES IN SOILS

A Thesis Presented

by

OLAF LEE WEEKS

Submitted to the Graduate School of the

University of Massachusetts

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 1974

Major Subject Soil Physics

# NONCONDUCTING PORES IN SOILS

A Thesis Presented

by

Olaf Lee Weeks

Approved as to style and content by:

Gordon L. Stewart
(Chairman of Committee)

F. M. Sandmann
(Head of Department)

Arnold Dean Adrian
(Member)

J. H. Baker
(Member)

# ACKNOWLEDGEMENTS

The writer wishes to extend his appreciation to his major advisor, Dr. Gordon L. Stewart, for his patience and guidance throughout this work.

Also thanks are extended to Dr. John H. Baker for his counsel on many occasions, and to Dr. D. D. Adrian for his interest in the study.

Acknowledgement is also made to the faculty, staff and all those who made this study possible.

# TABLE OF CONTENTS

# LIST OF TABLES

Page

# LIST OF FIGURES

Page

# INTRODUCTION

Traditionally, water movement in soils has been adequately described by Darcy's Law. This description is still very useful for many practical agricultural and engineering problems. Recent emphasis on ecological problems, brought about by the concern about the movement of solutions of nutrients and pollutants in soils, has resulted in attempts to describe more clearly water and solute movement in soils.

This more detailed approach confronts a very complex system which is not apparent from the terms in Darcy's equation. The system is made up of a distribution of particle sizes, which in turn constitutes a complex arrangement of pores of various sizes that are interconnected and make up a network of channels within the system. These pores act as conduits through which water and solutes move. Liquids moving through this interconnected network of channels are separated and later rejoined in such a way that neighboring liquid particles tend to become separated. This process is termed hydrodynamic dispersion, which is comprised of convection and diffusion components. Any particular pore available to transport flow carries a portion of the total flow, depending on its size, the tortuosity of flow path, roughness of the grains and other factors. The pores contain a nonconducting fraction of their total pore volume, termed nonconducting pores, which are made up of three parts: pores which are not continuous, termed "dead end"; pores which are very small and which carry such small amounts of flow

that they are essentially nonconducting; and the soil water-soil particle interface of large pores, where one finds a non-mobile boundary (of some thickness) of water not contributing to water movement.

These nonconducting pores in soils can be important in the detailed description of solute and water movement (as related to nutrient movement, leaching studies, recommended rates of effluent application in waste treatment operations, etc.), since the existence of nonconducting pores decreases the amount of pore space available for water flow and solute transport. It is the purpose of this study to investigate more fully the extent and characteristics of these nonconducting pores. This is accomplished in the laboratory using saturated columns and miscible displacement techniques, while varying soil texture, flow rate and time.

# LITERATURE REVIEW

## Historical

Early investigations involving water movement, conducted during the latter part of the nineteenth century, were concerned primarily with drainage as cultivation was the main interest of the agricultural work at this time. During the nineteenth century, because of the addition of new agricultural land brought under cultivation and the increased efficiency of farming, drainage became increasingly important.

The first quantitative study of water movement in porous media was that done by Henry Darcy (10) in 1856. While investigating the rate of water movement through vertical sand filters, he arrived at the equation describing water movement

$$q = kia$$

where $q$ = volumetric flow rate ($L^3/T$)

$k$ = hydraulic conductivity ($L/T$)

$i$ = hydraulic gradient ($L/L$)

$a$ = cross sectional area ($L^2$)

The study of soil moisture (not only related to drainage) was carried out by two Americans, E. W. Hilgard at California and F. H. King at Wisconsin. According to King, 1907, (20), water occurs in soils as gravitational, capillary, and hygroscopic water. He was interested in these three aspects of soil water and their relationship to crop growth. He described ways of expressing soil water content and methods of determining field capacity, and

the saturation and capillary capacity of soil. He investigated capillary rise and showed that the amount of water in soils, when a water table is present, depends on the height above the water table surface and the texture and structure of the soil. His experiments showed the heights to which water would rise by capillarity, and that the rate of rise is a function of water content. King described three types of water movement - gravitational, capillary and thermal. He carried out experiments describing vertical movement of water through shrinkage cracks, root channels, animal burrows and capillary pores.

King indicated that the movement of hygroscopic moisture is by evaporation. He speculated that moisture and temperature gradients caused movement of hygroscopic moisture.

Hilgard at California, 1919, (17) was interested in the rate and amount of absorption of moisture by soils and did a great deal of experimental work on the irrigation and drainage of soils. He also investigated the effect of quality of irrigation water on plant growth, with particular emphasis on salt content and the limiting concentrations of salt which are acceptable for crops.

Other early work on water movement in soils was conducted by the U.S.D.A. Bureau of Soils. Lyman J. Briggs, 1897, (6) presented a discussion on the Mechanics of Soil Moisture, in which he described the properties of water affecting its retention and movement in the soil. He discussed the influences of the properties of water and the porous media on the movement of water.

The other pioneer U.S.D.A. work was that of Buckingham, 1907, (7) in which extensive studies on evaporation from soils and the resulting moisture distribution led to a thermodynamic explanation of capillary action in soils. The partial differential equation describing capillary flow was presented and analogs of electric current and heat flow were compared with his capillary model. The various terms in the equation were defined and then methods of determining the value of these terms were discussed. The experimental results were then compared to the calculated ones.

Another important work was that of Slichter, 1905, of the U.S.G.S. (43) which gave perhaps the first experimental indication of the presence of hydrodynamic dispersion. While performing experiments during pumping tests on wells, he observed the spreading of a chloride tracer in these wells.

B. A. Keen (19) has an excellent discussion of the early approaches used in studying water movement.

The earliest miscible displacement study in soil solution appears to be the work done by Burd and Martin in 1923 (8). In their study of sandy and silty clay loams, they measured the electric conductivity of displaced solutions of soil water. They found no difference in conductivity of successive displaced solutions in these soils.

The early work by these men is significant because it is the basis on which all the subsequent investigations of water movement have been carried out. Other work dealing with water movement and dispersion has been carried out by petroleum and chemical

industries. Much of this available literature is quite theoretical in content and will not be discussed here.

## Miscible Displacement

Because of the complex nature of porous systems, a rigorous analysis of water movement is difficult. Therefore models are often used to try to explain the pertinent phenomena as it relates to a specific system. The most often used methods for these studies employ miscible displacement techniques. These consist of spiking a fluid with a tracer and then monitoring the concentration of the tracer as it moves through the system.

A brief review of general shapes and positions of breakthrough curves in miscible displacement studies is appropriate before reviewing the literature. The following is a brief review of Kirkham and Powers' (21) discussion of the topic.

Miscible displacement is a process where one fluid mixes with and displaces another fluid. This process as related to this study can be visualized by considering a pipe initially filled with a fluid which is being forced vertically up the pipe by a fluid entering from below. Initially there is a sharp interface between the two fluids but due to diffusion, viscous drag and eddies there is mixing between the two fluids, and the interface becomes less distinct. Of course mixing in soils will be different than mixing in a pipe, due to the complex geometry of soil particles and the interaction of pore shape and size.

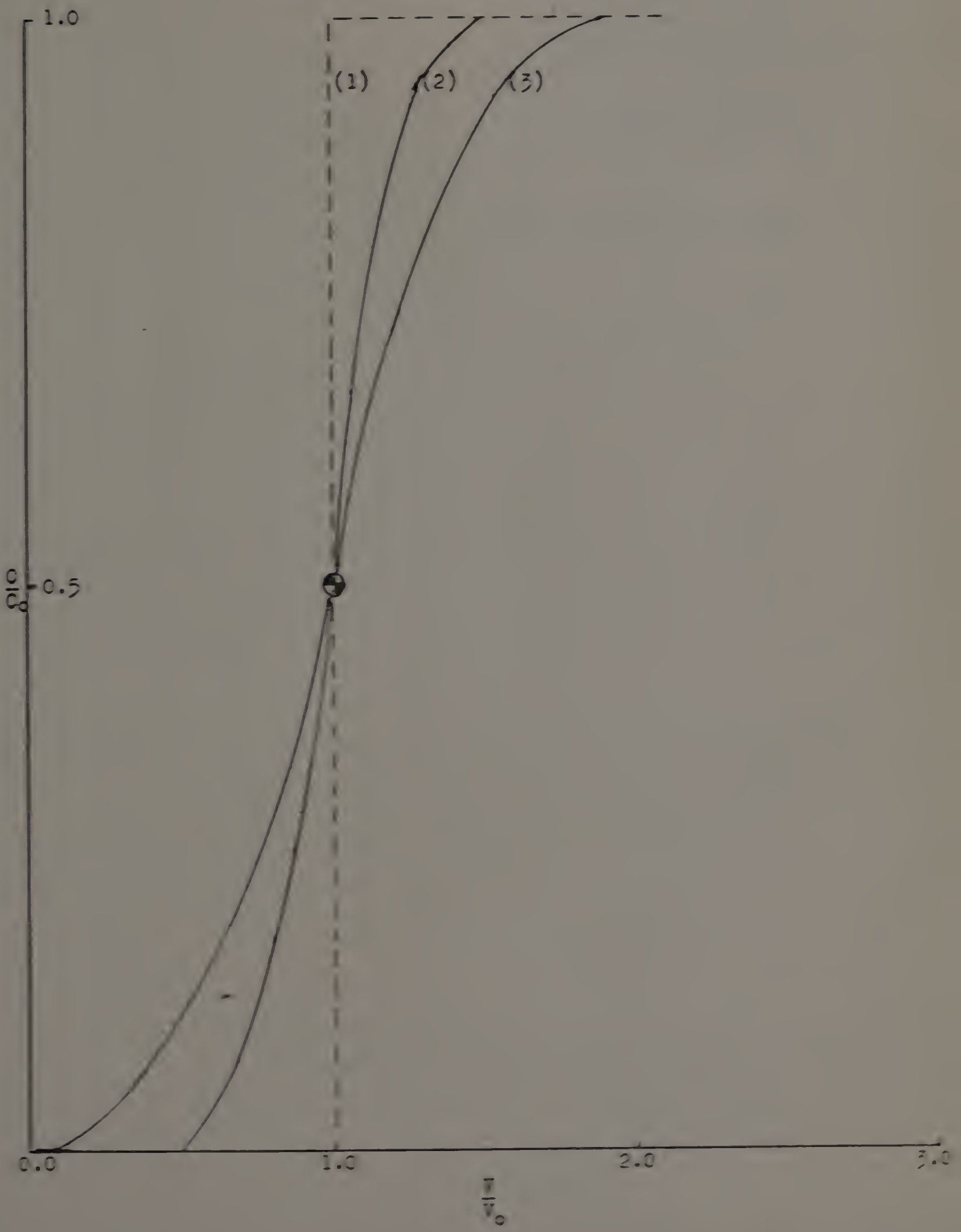
As one fluid displaces another, the concentration change of the displacing fluid is measured. A breakthrough curve consisting of a plot of the ratio $C/C_o$ versus pore volumes is constructed. $C/C_o$ will be zero at first and then approach one after some volume has been displaced. The number of pore volumes is equal to $V/V_o$ where V is the volume of effluent which has been pushed out of the column and replaced with a similar or different fluid, and $V_o$ is the volume of water filled pores in the porous media. In this study all columns are saturated so $V_o$ is the void volume of the column. Therefore a one pore volume displacement means that a volume of effluent equal to the void volume of the column has been pushed out of the column and been replaced by a similar or different fluid. A two pore volume displacement is where twice the void volume of the column has been pushed through the column and replaced by a fluid. This curve gives information about flow in the porous media.

## Hypothetical Breakthrough Curves

Figure 1 shows three breakthrough curves. Curve 1 is for piston flow, when there is no mixing and breakthrough occurs instantaneously. The velocity of the fluid is fast enough so the interface between the two fluids is stationary and, therefore, no diffusion or dispersion occurs across the interface. Curve 2 is more typical of soils. If no diffusion occurs in a system with a narrow range of high velocities, the curve will pass through $C/C_o = 0.5$ at one pore volume. Curve 3 is similar to curve 2,

FIGURE 1

HYPOTHETICAL BREAKTHROUGH CURVES



except that more mixing is occurring. The larger pores are displacing faster than the smaller ones and some diffusion may be occurring between small and large pores. The slopes of the curves compared to piston flow indicate the amount of mixing that has taken place.

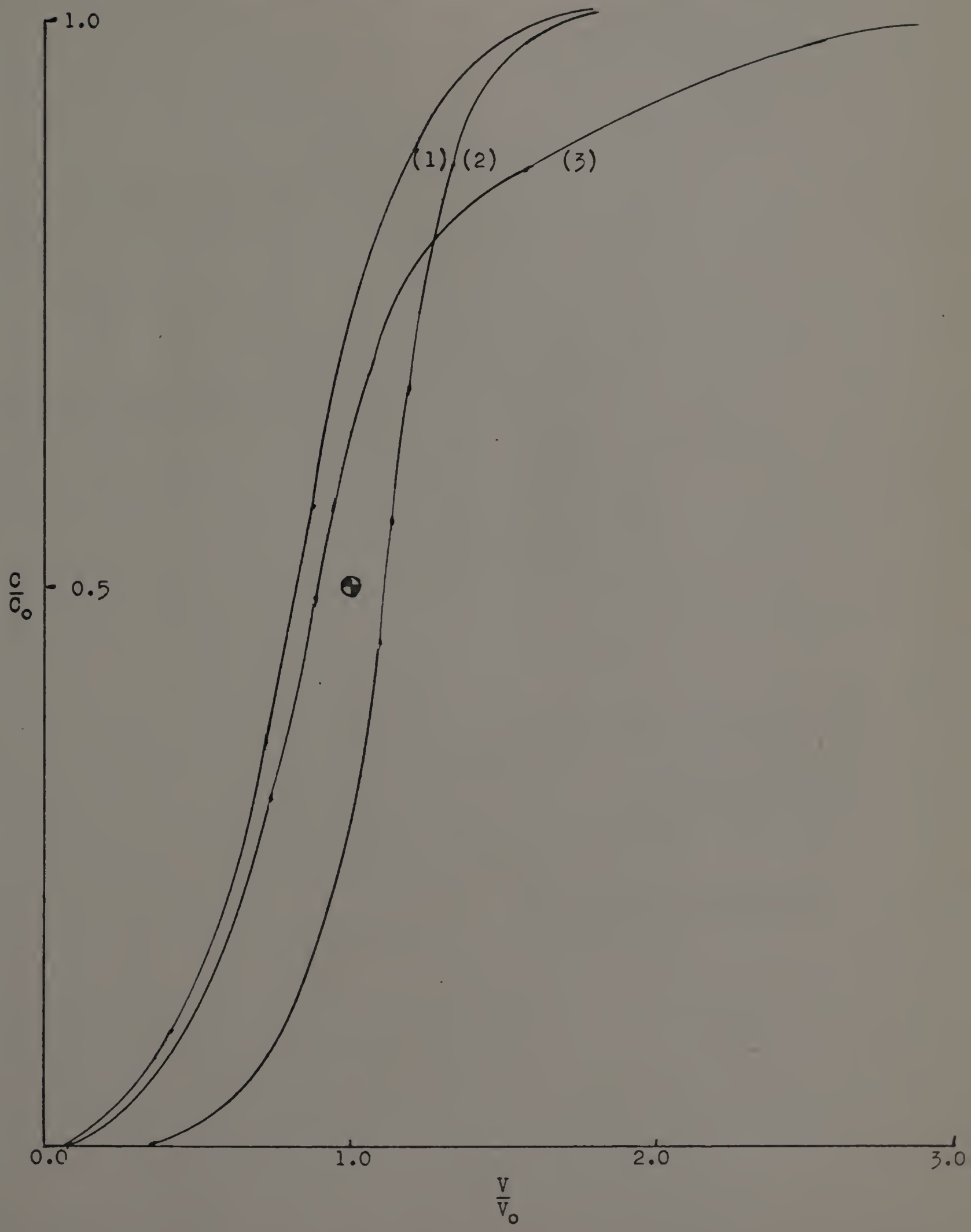
Three curves of the type found in the present study are shown in Figure 2. Curve 1 is shown shifted to the left of $C/C_o = 0.5$ at one pore volume, and this is referred to as exclusion. This shift in the curve, due to an early arrival of tracer, may be caused by channeling in the column or by nonexchange between conducting pores and water filled volumes. Part of the void volume of the column containing saturating solution has not been displaced by the displacing solution.

Curve 3 shows a condition termed "tailing off", shown by the flat slope at the end of the breakthrough curve. This is the result of nonequilibrium between the displaced and displacing fluids in the soil columns. Tracer diffuses or disperses out of the faster conducting pores into the slower conducting ones and then is displaced very slowly from these portions of the column. Tailing off often accompanies exclusion in the column, but not exclusively.

Curve 2 shows the breakthrough curve shifted to the right of $C/C_o = 0.5$ at one pore volume. This indicates that the tracer is being held back in the column. This holdback in the column could be attributed to exchange or precipitation in the column, mass difference of tracer and tracer solution, gravity in the case of

FIGURE 2

TYPICAL EXPERIMENTAL BREAKTHROUGH CURVES



vertical columns, and wide range of velocities coupled with diffusion. Nielson and Biggar (31) report that holdback is also observed when flow occurs at the soil-soil column interface. As tracer is held back a larger volume of effluent is required before tracer appears and the breakthrough curve is shifted to the right.

There are many aspects of miscible displacement techniques that are of interest. A primary concern is how well the tracer behaves in terms of its relation to the fluid it is tracing. The work of Kaufman and Orlob (18) describes the properties that an ideal tracer should have. They suggest that the tracer should describe variations of velocity of the liquid being traced without changing the transmission characteristics of the porous media; the tracer should be detectable in low concentration to minimize changes in porous media structure or liquid properties which might change the permeability of the porous media; and that there should be no absorption or ion exchange of tracer by the solid phase. They tested a number of organic, inorganic and radioactive tracers to determine which ones came the closest to fulfilling these criteria. They concluded that, although each tracer has its own limitations, chloride was the most ideal. The most commonly used tracer in miscible displacement studies in the past has been chloride, but not all investigators share the idea that chloride is the best tracer.

Thomas and Swoboda (44) indicate that in leaching studies chloride ions move much faster through soil, due to anion exclusion effects, than does the soil solution. Other investigators indicate

the same finding. Stewart (41, 42) at Massachusetts found that tritium is a very good tracer to use for miscible displacement studies. The concentrations of tritium required for adequate monitoring of flow are much less than required for nonradioactive tracers such as chloride. A disadvantage in using tritium for microscopic solute transport studies in clay is isotopic exchange and the possibility of an isotopic effect, but for most transport studies isotopic interaction is negligible when compared to other experimental errors. Presently chloride and tritium appear to be the most widely used water tracers in hydrologic systems.

Other aspects of miscible displacement studies that have received considerable attention need to be discussed. Perhaps the most complete work on miscible displacement in soils, although not the first, is that of Biggar and Nielson (2, 3, 31, 32, 33). They introduced many parameters into their study, and explained the effects of these parameters by means of breakthrough curves.

They attributed the movement of tracer, and subsequently of the soil solution, to the processes of convection, diffusion and chemical reaction. By varying velocities in saturated soil columns and observing the shape and position of the breakthrough curves, they could indicate the dominating process (convection, diffusion, chemical reaction). Differences in soil texture and structure could be explained from the breakthrough curves when run at the same velocity.

By varying the water content of the columns and running similar studies, they concluded that breakthrough curves for

unsaturated soils give more information about microscopic flow than breakthrough curves for saturated soils, because the larger pores are drained and an increased amount of void space does not contribute to water flow.

Their investigations included studying the behavior of chloride and tritium tracers (2). Expanding on the work of Handy (16), who showed that the diffusion rates of chloride and tritium were unequal, they used the two tracers to determine the contribution of diffusion to the dispersion process. If the breakthrough curves are the same for the two tracers, they conclude that convection predominates. If the curves are different, then the tracer with the greater diffusion coefficient will appear later, due to more complete mixing in the column. If the difference in the diffusion coefficients is much greater, then not only would more complete mixing occur but also the tracer with the greater diffusion coefficient will breakthrough earlier. They indicate that the degree of saturation affects the position and shape of the breakthrough curve when tracers are used to determine source, direction or velocity of water. The effect of soil aggregation on the characteristics of the breakthrough curves was studied by comparing the breakthrough curves of different size aggregates and also glass beads (non-aggregated) under saturated conditions. It was noted that as aggregate size increased, the curves changed their shapes from the skewed sigmoid and became more concave to the abscissa, and also shifted to the left. Also the tracers appeared earlier and required more throughput volume to reach $C/C_o = 1.0$

Some of the more common mathematical models which had been suggested for studying miscible displacement in horizontal columns were briefly reviewed (32). Each one was examined and the assumptions required for its use were explained. Then miscible displacement data obtained from glass bead media was investigated (33) in order to compare the mathematical models. The diffusion and dispersion equations which were introduced in the theoretical review were used to fit the data. Nielson and Biggar (33) found that the diffusion equation represented their experimental data better than the dispersion equation.

The last part of Biggar and Nielson's (3) work involved investigation of the exchange processes with soil. Chloride and magnesium ions were used as tracers in this experiment, and the results were compared. Under saturated conditions, velocities were varied and the breakthrough curves compared. The chloride curve almost passed through $C/C_o = 0.5$ at one pore volume, while the magnesium curve passed far to the right of this point, due to the exchange with the soil. Diffusion effects were more noticeable at the lower velocities. Concentrations of magnesium were changed, and the smaller concentrations required more throughput to reach one pore volume. In unsaturated conditions, the chloride breakthrough curve shifted to the left of one pore volume, but a corresponding shift for magnesium did not occur. The shape of the magnesium breakthrough curve for the saturated and unsaturated condition is not the same, the unsaturated curve being shifted further to the right of $C/C_o = 0.5$ at one pore volume and the shape

of the curve being less sigmoid. Biggar and Nielson (3) compared their experimental results to theoretical models which had been applied to chromatographic studies. In both saturated and unsaturated conditions the models were found to be inadequate because of difficulties in evaluating parameters in the equations. Physically the difficulty involves non-equilibrium between the exchange sites and the displacing fluid. However, the characteristics of breakthrough curves do not depend entirely on exchange but also on diffusion and convection. Therefore, all or combinations of these three processes need to be considered together in the models to get agreement with the experimental data.

A number of investigators have studied diffusion in soils and have developed methods of determining quantitatively this process in soil systems. Porter et al. (37) studied chloride diffusion in soils and the influence of water content on diffusion. They took Fick's law of diffusion and modified it to account for a porous media by introducing a geometric factor due to path and tortuosity, and an interaction factor due to viscosity and ion exchange. Because a steady state diffusion experiment is difficult to set up, a transient study was run on the basis of Fick's second law. They gave a solution for the second law, along with appropriate boundary conditions. Chloride diffusivities, measured on medium and fine textured soils at various moisture contents, were divided by the diffusivity of chloride in water, which gave what the authors called a "transmission factor." The transmission factor, plotted as a function of moisture content, gave straight lines. The transmission

factor was discussed in relation to viscosity effects, interaction with soil particles, and tortuosity of pores.

Nakayama and Jackson (30) studied diffusion of tritiated water in soils. Using Fick's second law, a solution was derived for the apparent diffusion coefficient. The diffusion was then measured for four soil materials and glass beads. It was found that for water contents between 40 and 10 percent, the diffusion coefficient was constant. Below 10 percent the diffusion coefficient rose to a maximum and then dropped off at very low moisture contents.

Other investigators have studied hydrodynamic dispersion in soils. Day and Forsythe (11) indicated that the spreading of solute is proportional to the square root of the linear displacement of fluid. The proportionality constant is characteristic of the soil, independent of velocity and determined empirically. As a result, solute movement cannot be accounted for by average velocities, and a proportionality constant to account for dispersion must be considered. They suggest that diffusion is an independent process, is superimposed on dispersion, but is important at very slow velocities or in motionless liquid.

Scheidegger (40) theoretically determined that dispersion (D) is related to velocity by either

$$D = \alpha q$$

$$\text{or } D = \alpha q^2$$

where $\alpha$ = proportionality constant
$q$ = velocity cm/sec

Experimental work indicates that dispersion is directly proportional to velocity.

Blackwell et al. (5), working on miscible displacement on the scale of petroleum reservoirs (macroscopic), indicate that dispersion is independent of flow rate and that only ordinary diffusion needs to be considered.

Rose and Passioura (38) present a method of analyzing experiments in hydrodynamic dispersion based on the logarithmic normal transformation of a numerical solution of the equation of longitudinal dispersion in a column of finite length. If the experimental data satisfies the analysis, they fall on a straight line, which is a function of the Brenner number. They suggest that deviations from the analysis are attributable to non-uniform flow.

Other work on miscible displacement has been done by Krupp and Elrich (23) and Elrich and French (13), and is similar to some of the previous work discussed. Krupp and Elrich (24) did study density effects in miscible displacement studies. The criteria used to determine if the flow in a vertical column is stable or not is expressed as a critical velocity, which is proportional to the ratio of the difference in density to the difference in viscosity of the liquids under consideration. The effects of velocity, density and viscosity were seen in the breakthrough curves. It was noted by them that density was more significant than viscosity in altering displacement. Their study involved the displacements of distilled water and chloride solutions. Rose and Passioura (39) conducted a similar study using chloride solutions and distilled water, and showed differences in breakthrough curves due to gravity effects.

A similar study to that of Rose and Passioura involving gravity segregation was not found for the tritium tracer. In this present

study, which uses a vertical column, the author feels that a gravity effect is present and causes a holdback of the tritium on the breakthrough curve. However, due to the very small concentrations of tritium used in this work, it is doubtful that the above methods of analysis can be used in this study. The viscosity and density difference are present but are so small that an accurate measurement is doubtful. It is of interest here to try and apply some type of a correction to the breakthrough curves to account for this gravity effect. This correction will be discussed later.

For more detailed treatments on the mathematics of miscible displacement experiments, Olsen and Kemper (35), Kirkham and Powers (21) and Bear (1) are good references.

The studies which have been referred to in this section are of importance in the present study and should be kept in mind in the analysis of the results.

## Nonconducting Pores in Soil

The investigations of nonconducting pores in soils have been carried out on both a theoretical and experimental basis. The models used to account for nonconducting pores have been of various types. They generally involve an equation describing dispersion of solute, with an additional term added to describe "dead end" space.

Turner (45) describes a differential capacitance model for dispersion which is subjected to a sinusoidal varying concentration of solute. In his model there are two components of the pore, the main channel and a distribution of side pockets of prismatic cross section. This model has not been particularly satisfactory

for soil investigations, because of the restrictions placed on the stagnant areas of fluids. Lapidus and Amundson (27) have derived a solution to this same model.

Coates and Smith (9) have compared dispersion in porous media by a simple diffusion model and by a differential capacitance model which had been previously described by Deans (12). Deans used a finite stage model which involved three parameters - number of stages, amount of stagnant volume, and a rate constant for mass transfer into the stagnant volume. Using this approach and fitting it to the experimental data, the amount of stagnant volume can be determined.

Rose and Passioura (38) have reviewed much of the experimental work in hydrodynamic dispersion. Repeating the previous work of Coates and Smith, they indicate that the apparent correlation between the theoretical data and the experimental data is due to channeling through the soil column because of poor packing or to an improper distribution of flow as a result of poor contact at the interface between the soil and retaining plate. These conditions result in an early breakthrough curve which tails out at the end due to a slow equilibrium between the stagnant volume and the rest of the solution. If they are correct, then the amount of dead end pores reported by Coates and Smith is too large.

Marshall (28) and Millington and Quirk (29) each developed equations whereby they could calculate saturated or unsaturated Poisouille permeability of a porous media. These were computed from a knowledge of the pore size class distribution, which are

obtained from moisture retention data. Values computed compared favorably to previously published experimental results.

Kunze et al. (25) modified Millington and Quirk's equation and came up with better agreement between calculated and experimental values. Green and Corey (14) working on a similar study at Hawaii, obtained results supporting Kunze et al. Green et al. (15) expanded on this method of calculating total conductivity and used it to calculate the conductivity of each individual pore size class for two soils. These partitioned conductivities of each pore size class were then divided by the appropriate volumetric water content fraction, which gave conductivity values expressed on a pore velocity basis. This then gave the relative capacity of each pore size class to conduct water, and, therefore, an estimate of the percentage of pores which would contribute to water flow. From the results of their studies on two Hawaiian soils they concluded that 50 percent of the pores contributed to water flow and 50 percent did not.

Orlob and Radhakrishna (36) in studying the effect of entrapped gases on the hydraulic characteristics of porous media explain how the breakthrough curve can be used to estimate the fraction of the pore volume participating in the flow. Their approach involved this relationship:

$$fe = \int_{o}^{\infty} \left(1 - \frac{C}{C_o}\right) d\left(\frac{V}{V_t}\right)$$

C = concentration of solute

$C_o$ = maximum concentration of solute

V = volume

$V_e$ = effective volume

$V_t$ = total volume

where fe = $\frac{V_e}{V_t}$ = effective porosity

and therefore

(1-fe) = stagnant volume

Kissel et al. (22) at the Texas Experiment Station performed infiltration studies on disturbed and undisturbed swelling clay soil. Chloride salt and a phosphorescent material were used to run breakthrough curves. Using a black light and chemical methods for chloride determinations, definite flow patterns appeared in the soil columns. They were particularly noticeable at shrinkage cracks and large connecting pores. The breakthrough curves for the columns were plotted and the value for the pore volume at $C/C_o = 0.5$ was used to estimate the percentage of the column which conducted and the percentage which did not conduct. They found for their soil that 60 percent of the pores did not conduct solute and 40 percent did.

The work of Kissel et al. and Green et al. indicates that a substantial amount of pore space does not contribute to water movement. In contrast, Coates and Smith indicate a smaller quantity not contributing. It is the purpose of this study to try and determine the amount of pore space in several different porous media which is not exchangeable with a displacing solution and see if the previously reported values reflect primarily a nonexchangeable pore space or a slowly conducting pore space.

# MATERIALS AND METHODS

## Soils

To measure the nonconducting (those pores not exchanging with tracer) pore space in soils under conditions of complete saturation and variable soil texture, fluid velocity and time, procedures were used as described in detail elsewhere (4, 26, 34) except as noted below. Four Massachusetts soils were used, three being sandy loams and one an aggregated clay loam:

a. An unidentified sandy loam

b. Hadley fine sandy loam; a well-drained member of a coarse-silty mixed mesic family of Fluventic Dystrocrepts

c. Windsor loamy fine sand; a member of an excessively drained mixed mesic family of Entic Haplosthods

d. Buxton loamy sand; a member of the moderately well-drained highly aggregated fine mixed mesic family of Aquic Dystric Entrocrepts

In addition, an aggregated montmorillonite, heated to 700° C, and an Ottawa sand were used. The mechanical analysis of the soils are shown in Tables 1 and 2, and moisture retention data in Table 3. It was desired also to use a silt loam, but at the time the soils were collected a silt loam was not easily located. However the three sandy loams were used to satisfy the different textural requirements. The clay mineral montmorillonite was heated to 700° C to destroy the hydroxyl groups of the crystal lattice. Heating reduced the number of tritium exchange sites,

TABLE 1

GRAIN SIZE OF CERTAIN SOILS* AS DETERMINED BY PIPETTE ANALYSIS, BULK DENSITY AND VOID VOLUME

| Soil | Bulk Density of Column | Void Volume of Column c.c. | Percent Greater than 2 mm. Sieve | Percent Coarse Sand | Percent Fine Sand | Percent Silt | Percent Clay | Percent Loss by Solution |
|---|---|---|---|---|---|---|---|---|
| 1 Unidentified Sandy Loam | 1.35 | 110.76 | 0.00 | 32.4 | 57.2 | 10.4 | | 3.5 |
| 2 Buxton Aggregated Clay Loam | 1.07 | 134.73 | 0.00 | 6.48 | 20.08 | 46.23 | 29.20 | 5.69 |
| 3 Hadley Fine Sandy Loam | 1.31 | 114.61 | 0.50 | 6.54 | 53.34 | | 9.08 | 3.78 |
| 4 Windsor Loamy Sand | 1.73 | 79.37 | 3.95 | 67.64 | 18.90 | 12.13 | 10.11 | -- |
| 5 Ottawa Sand | 1.84 | 70.00 | | | | | | |
| 6 Preheated Montmorillonite Aggregate | 1.24 | 119.81 | | | | | | |

*All soils were low in organic matter.

TABLE 2

GRAIN AND AGGREGATE SIZE AS DETERMINED BY SIEVE ANALYSIS*

| Mesh Sieve Size | Percent Soil Finer Than | | |
|---|---|---|---|
| | Ottawa | Montmorillonite 700°C | Windsor Loamy Sand |
| #10 | - | 100.00 | 96.33 |
| 15 | - | 99.97 | 87.70 |
| 30 | 64 | - | - |
| 35 | — | 54.47 | 56.39 |
| 40 | 14 | - | - |
| 50 | 9 | - | - |
| 60 | - | 6.13 | 23.81 |
| 140 | - | 1.97 | 12.95 |
| Base | 0 | 0 | 0 |

*Dashes (-) indicate that the particular sieve size was not used.

TABLE 3

MOISTURE RETENTION FOR FIELD SOIL, COARSE SAND, AND A CLAY MINERAL

| Tension | Water Content - $cm^3/cm^3$ | | | | | |
|---|---|---|---|---|---|---|
| | Unidentified Sandy Loam | Buxton Aggregate Clay Loam | Ottawa Sand | Windsor Loamy Sand | Hadley Fine Sandy Loam | Preheated Montmorillonite Aggregate |
| 0-10 cm water | .63 | .65 | .42 | - | 1.36 | .69 |
| 10-20 cm water | .61 | .58 | .29 | .50 | .64 | .57 |
| 20-100 cm water | .51 | .35 | .011 | .19 | .60 | .20 |
| 1/3 atm. | .27 | .29 | .011 | .17 | .51 | .19 |
| 1 atm. | .27 | .29 | .0055 | .156 | .49 | |
| 2 atm. | .07 | .19 | 0 | .07 | .12 | |
| 4 atm. | .07 | .16 | 0 | .06 | .09 | |

eliminated the swelling property of this material and produced a stable aggregate.

## Preparation of Soils and Packing the Columns

The soils were oven dried at a temperature of 110° C for approximately twenty-four hours, and then immediately transferred to a desicator where they remained until reaching room temperature.

The column used was made from a plexiglass plastic tube 4.44 centimeters inside diameter and 14.6 centimeters long (Figure 3). Near the bottom of the column a coarse sintered glass porous disk was fitted into a shoulder cut into the plastic. The void volume of the disk was 5 milliliters. A reservoir area with a venting hole was placed below the disk. The top of the column was open to the atmosphere and had a spout to direct the effluent into a sample collector.

The column was placed vertically into a vibrator packing machine (Figure 4) equipped with vibrators and a tremie drive mechanism to deposit the soil in the column. The soil column was packed by introducing a funnel with a long stem into the column and resting it on top of the porous disk. A motor withdrew the funnel at a constant rate while the dry soil was being deposited into the column. Soil was packed evenly up to the bottom of the spout. Simultaneously with the filling of the column with soil the vibration was carried out by means of a vibrator connected to a variable speed rheostat. Care was taken to vary the vibrational frequency to avoid setting up nodes of vibration and

FIGURE 3

DIAGRAM OF MISCIBLE DISPLACEMENT APPARATUS

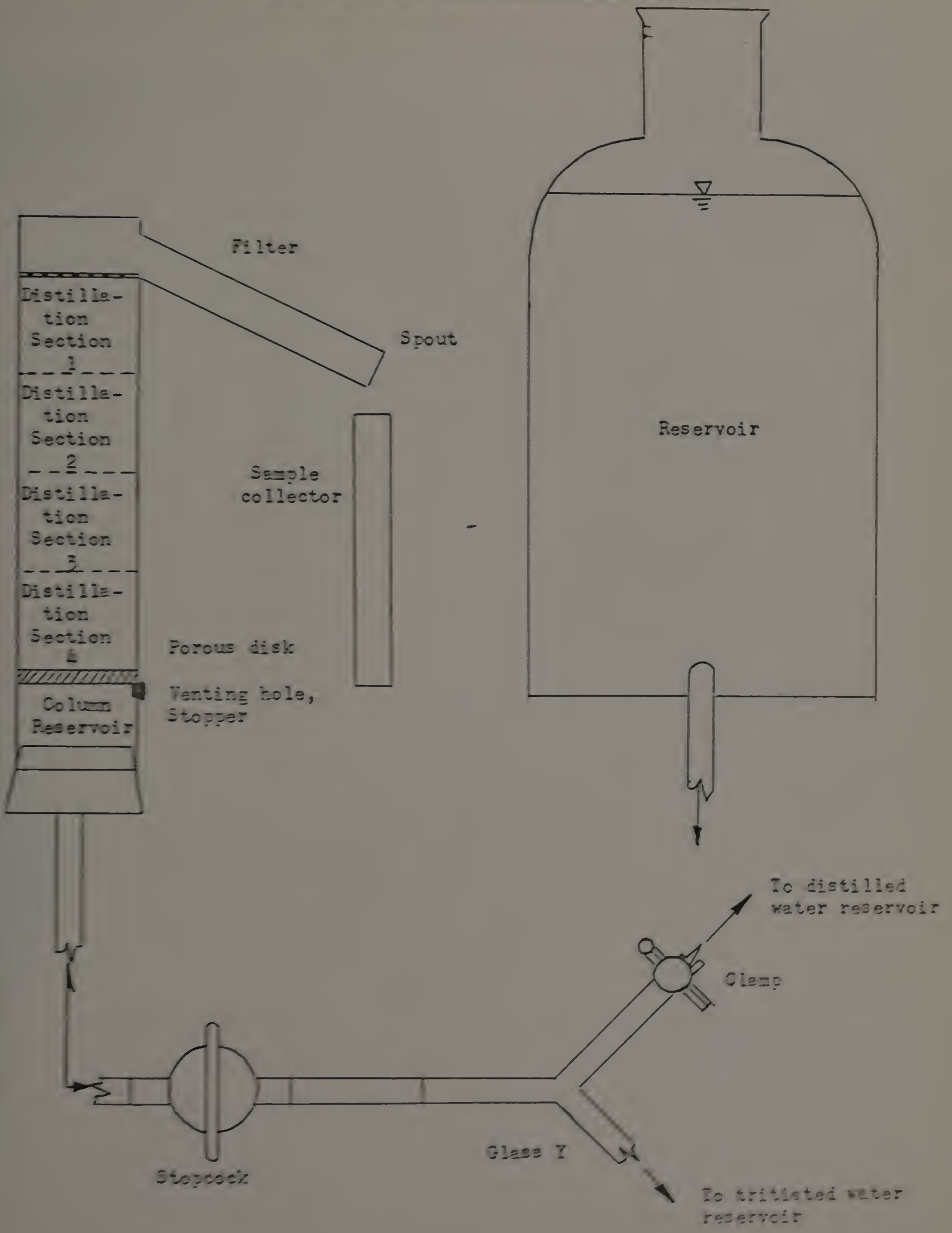


FIGURE 4

VIBRATOR PACKING MACHINE

possible density variations over the length of the column. With the finer textured soils a final sieving was obtained by using a No. 18 wire mesh screen attached to the end of the funnel stem. This reduced the tendency of the particle sizes to segregate as they are deposited. This screen was not used for the coarser soils.

Prior to packing the soil, samples were weighed to give a predetermined bulk density when packed in the column. The bulk density for the different soils is shown in Tables 1 and 2. The bulk density obtained was at or near the maximum attainable for the packing procedure used. This was desired, since they would represent more closely the subsurface soil deposits, with their generally corresponding smaller pore size.

After the packing was complete, the column was removed and a filter placed over the top of the soil just even with the spout. The filter used consisted of two No. 18 wire mesh screens, 4.44 centimeters in diameter, with a single thickness of cheese cloth sandwiched between them. This was to help prevent fine particles from being carried out with the effluent and into the sample collector. A suspension of soil particles often appeared as a cloudy suspension in the first few aliquots of the displaced fluids. The particulate materials in the effluent are undesirable because of possible quenching of the tritium count, and every effort was made to eliminate them. This problem will be discussed later.

Over the filter a rubber stopper, containing a relief port, was placed to seal the upper end of the column. The stopper was secured to the column. After this preparation, the column was placed in a water filled wacuum desicator. The air in the desicator was removed with a vacuum pump, and the soil column was left in this state to deair and until saturation was reached. The purpose of the rubber stopper was to allow the air in the soil to escape and at the same time keep the soil in the column from splitting apart. This setup is shown in the photograph in Figure 5.

The water in the vacuum desicator used to completely saturate the soil columns was in some cases distilled, deaired water with 25 ppm chlorox, and in others distilled, deaired water spiked with tritium and 25 ppm chlorox. The activity of the tritium was $7.2 \times 10^{-9}$ curies/ml, which was the same as the water used in the displacements. The chlorox was added to prevent the growth of mold and other organisms in the column and in the collected effluent.

## Displacements

The soil column upon reaching saturation was removed from the desicator and clamped into position on the sample collector, and the displacement reservoirs were connected to the bottom of the column. The two displacement reservoirs (one containing tritiated water, the other containing distilled water) are connected to the column by means of a glass Y, a stopcock and a flexible tubing connected to a rubber stopper. The rubber stopper

FIGURE 5

SATURATION APPARATUS

was fitted snugly into the bottom of the column, creating the column reservoir. Pinch clamps connected to the separate lines allowed or stopped flow, depending on which reservoir was desired, and also allowed the lines from the glass Y to the stopper to be flushed.

The reservoir containing the fluid used in the saturation was connected to the column by opening the pinch clamp and stopcock. Flow was initiated by a pressure difference obtained by placing the displacement reservoir to give the desired head. The venting hole next to the porous disk was left open until the air in the column reservoir was displaced by the fluid, and then closed by inserting a cork stopper. Flow being initiated, saturated hydraulic conductivity tests were run. After the hydraulic conductivity tests were run, the displacement tests began. The open pinch clamp on the saturating fluid reservoir was closed. The cork from the bottom of the soil column was then removed to allow the column reservoir to be quickly drained. The line between the glass Y and the rubber stopper was flushed by opening the pinch clamp on the other reservoir and allowing flow to occur. The stopcock was then closed, the rubber stopper reinserted and the stopcock opened. The column reservoir filling was carried out again.

Each displacement experiment was carried out by positioning the displacing reservoir to give the desired head. The spout on the column was positioned so the effluent was caught by the sample collector. Saturated hydraulic conductivity tests were also made

during the displacement run. The sample collector used was a volumetric fractionator. The displacement setup is shown in the photograph in Figure 6.

After the desired number of pore volumes were collected, the displacing reservoir was disconnected and the breakthrough aliquots were set aside. The soil was removed from the column intact and then sectioned in quarters (section number shown in Figure 3), numbering from top to bottom. Samples of each quarter were then placed in test tubes. Glass wool was placed over the soil in the test tubes and both packed tightly into the bottom of the tubes. These sections were then vacuum distilled at 110° C until dry. The setup for the vacuum distillation is shown in the photograph in Figure 7. It consisted of a heating block which heated the samples to the desired temperature. Test tubes containing soil samples were positioned in the heating block, connected to a vapor collecting tube which was immersed in a dry ice and alcohol solution, which in turn was connected to a vacuum pump. These distilled water samples were saved for later tritium analysis.

The breakthrough aliquots and the distilled water samples were counted, using a liquid scintillation spectrometer and a toluene base counting cocktail.

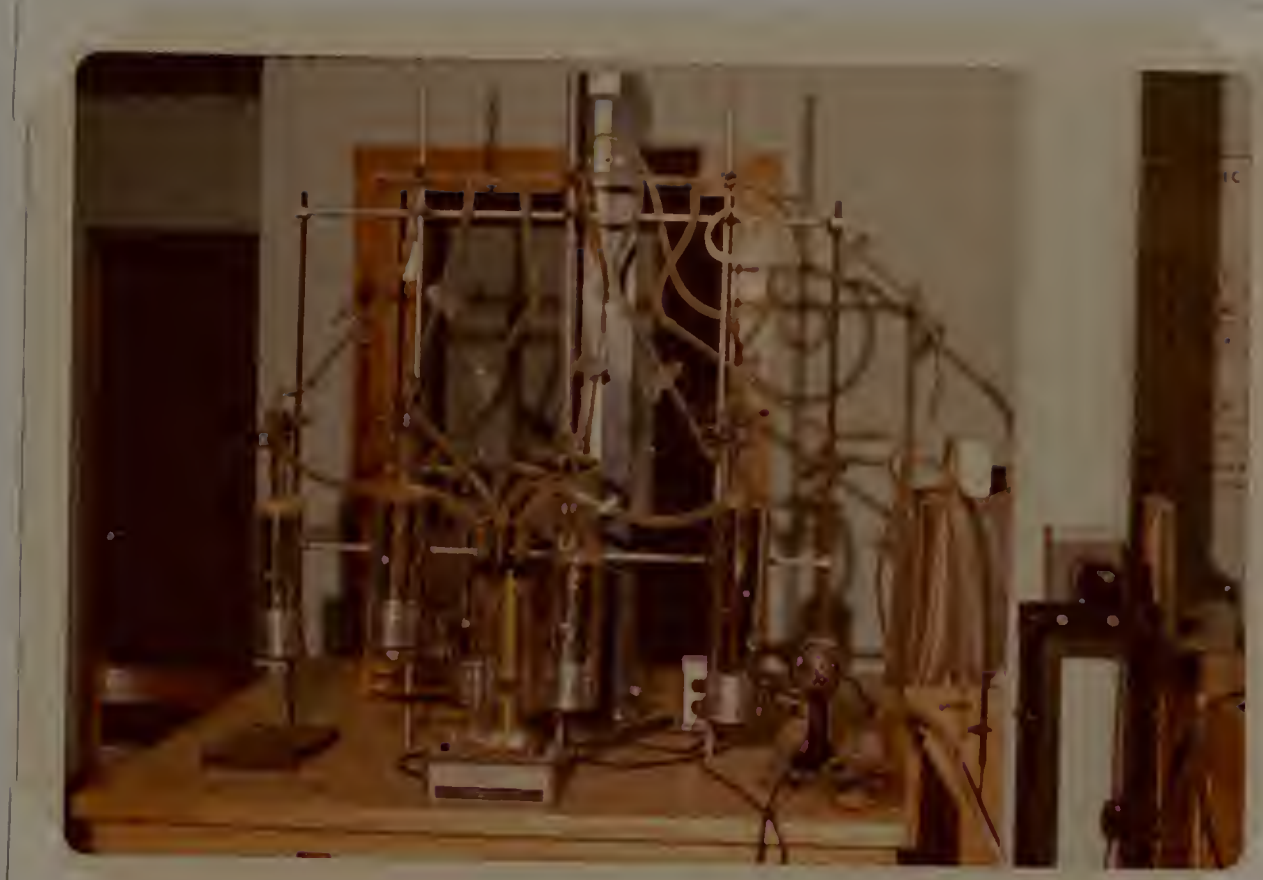
The amount of exchange taking place between the soil particles and the tritium tracer was estimated from an independent equilibrium study. A paste was made by saturating the different soils with tritiated water. This mixture was allowed to equilibrate. Then portions of the soil samples were packed into Vycor glass tubes, connected to a vacuum distillation line, placed in a furnace and

FIGURE 6

DISPLACEMENT APPARATUS

FIGURE 7

VACUUM DISTILLATION APPARATUS



then heated. The vacuum distillation system was used to collect the water given off at temperatures of 110° C, 300° C and 800° C. The water coming off at 110° C is bulk pore water, that coming off at 800° C is crystal lattice hydroxyl water, and that coming off at 300° C is tenaciously adsorbed water and weakly bound crystal lattice hydroxyls.

At each temperature the water given off was collected in a dry ice alcohol cold finger trap and removed. These samples were also counted on the liquid scintillation spectrometer. The data in Table 4 shows the amount of water coming off at the different temperatures and the degree of isotopic exchange with crystal lattice hydroxyls. The $\frac{T_{300-800}}{T_{110}}$ ratio is the fraction of the crystal lattice hydroxyls which exchanged with the bulk pore water. $\frac{T_{110-300}}{T_{110}}$ is the fraction of weak crystal lattice hydroxyls and adsorbed water which exchanged with bulk pore water.

Horizontal displacements were made on three of the soils used in this study. The preparations of the soil and columns were the same as for the vertical ones. The only difference between them was the size of columns used. The horizontal columns were made from disks 3 centimeters long and 2.68 centimeters inside diameter, taped together to give an overall length of 14.6 centimeters length. Instead of one end being open, both ends were covered with a medium coarseness disk, which was inset into the disks. Displacements, distillations and counting procedures were the same as for the vertical columns.

TABLE 4

TRITIUM EXCHANGE WITH CRYSTAL LATTICE HYDROXYLS OF FIELD SOILS

| | Unidentified Sandy Loam | Buxton Aggregated Clay Loam | Hadley Fine Sandy Loam | Windsor Loamy Sand |
|---|---|---|---|---|
| Wt. of soil dry | 69.12 | 61.68 | 61.90 | 126.68 |
| Wt. of water at 110° C | 25.32 | 26.93 | 26.62 | 23.62 |
| Wt. $H_2O$ @ 300° C | .50 | 0.50 | .42 | .66 |
| Wt. $H_2O$ @ 800° C | .39 | 1.01 | .69 | .61 |
| $\frac{T_{110-300}}{T_{110}}$ | .35 | .58 | .43 | .32 |
| $\frac{T_{300-800}}{T_{110}}$ | .21 | .23 | .20 | .20 |

# RESULTS AND DISCUSSION

## Soil No. 1

### Unidentified Sandy Loam

In order to establish a reference point for the procedure used in the laboratory determination of nonconducting pore space in field soils, an unidentified sandy loam available in the laboratory for various types of studies was used. During the summer of 1973 columns were prepared as described under Materials and Methods, and duplicate volume displacements of one, two and three pore volumes were made at a single velocity. The breakthrough curves are shown in Figure 8 and the distillation data is in Table 5. The average displacement velocity calculated from Darcy's Law was 1.89 cm/hr, the maximum rate attainable for this soil with existing equipment.

The slope of the breakthrough curve for the vertical columns starts to rise very sharply at 0.9 of a pore volume. It rises at a slope of 4 to 1, and at 1.25 pore volume starts to flatten out and reaches $C/C_o = 1.0$ at 1.80 pore volume. The steep slope of the curve indicates that relatively little mixing occurred between the displaced and displacing fluid. No tailing off is observed, which indicates that equilibrium was established within the primary conducting pores of the column. The most noticeable aspect of this curve is that it is shifted approximately 0.12 of a pore volume to the right of $C/C_o = 0.5$ at one pore volume. This shift of the curve to the right was expected because previous investigations show a

FIGURE 8

BREAKTHROUGH CURVES FOR UNIDENTIFIED SANDY LOAM

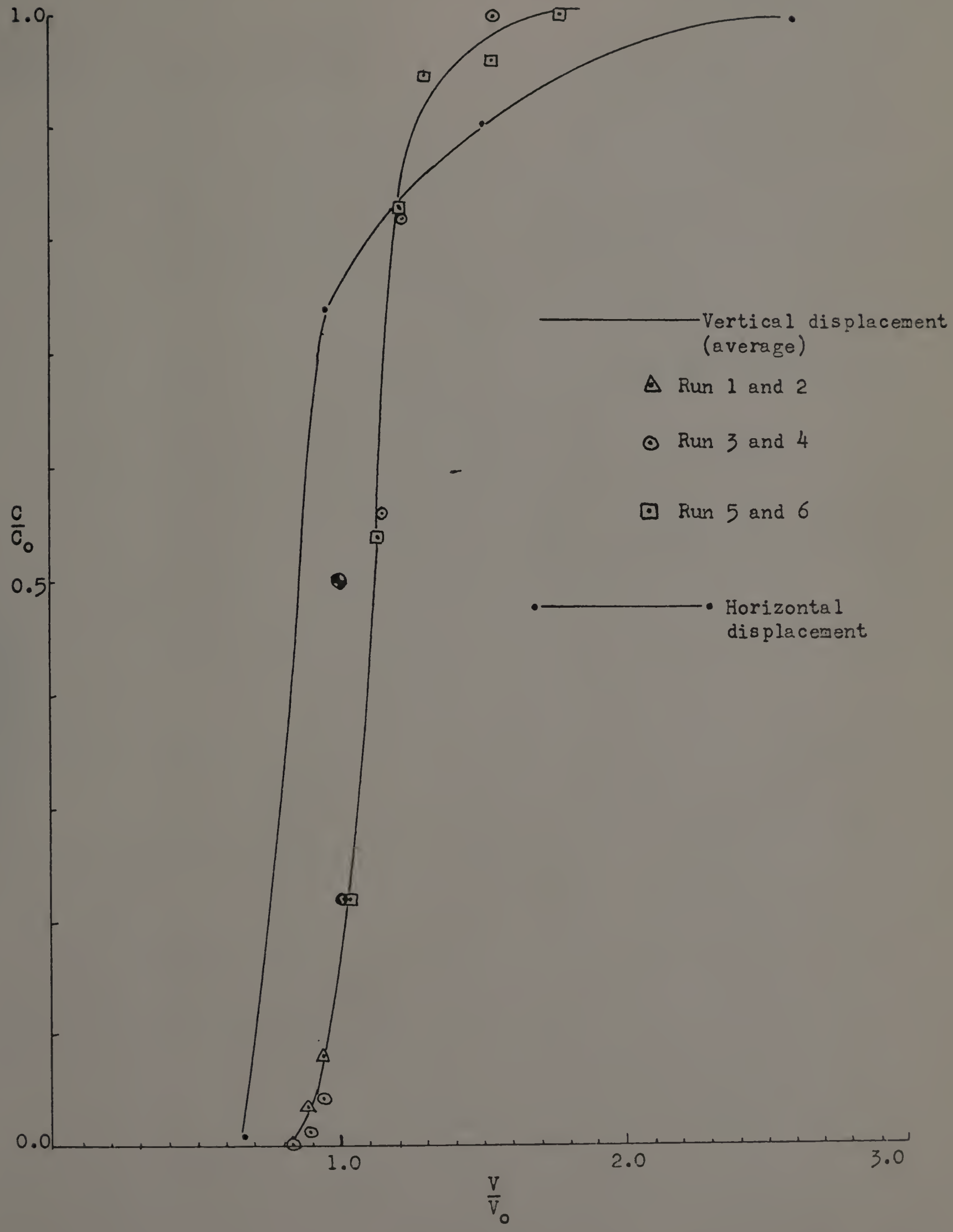


TABLE 5

EFFECT OF DIFFERENT PORE VOLUME DISPLACEMENTS AND COLUMN ORIENTATION ON THE PERCENT NONCONDUCTING PORES IN AN UNIDENTIFIED SANDY LOAM RUN AT A 29 CM HEAD WITH TRITIATED WATER DISPLACING DISTILLED WATER

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Pore volumes displaced | 1 (vertical) | 1 (vertical) | 2 (vertical) | 2 (vertical) | 3 (vertical) | 3 (vertical) | 3 (horizontal) |
| Displaced - displacing solution | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO |
| Bulk density g/cc | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.35 | 1.47 |
| Head $\Delta H$ cm | 29 | 29 | 29 | 29 | 29 | 29 | 29 |
| Velocity cm/hr | 1.67 | 1.55 | 1.76 | 1.80 | 2.05 | 2.52 | 1.69 |
| Section No. | Percent Nonconducting Pores | | | | | | |
| 1 | 63.0 | 45.0 | 7.3 | 4.6 | 5.2 | 6.5 | 0.0 |
| 2 | 30.7 | 9.8 | 6.6 | 5.7 | 4.8 | 3.7 | |
| 3 | 16.0 | 5.6 | 6.9 | 4.5 | 5.5 | 5.1 | 1.0 |
| 4 | 10.5 | 6.0 | 3.7 | 6.4 | 6.0 | 2.5 | 0.0 |
| 5 | 7.5 | 6.0 | 2.7 | 6.4 | 5.3 | 4.8 | |
| 6 | 8.8 | 5.0 | 5.4 | 12.9 | 5.1 | 5.7 | (only 5 sections) |

shift (31) but its magnitude was greater than anticipated. A shift to the right in the breakthrough curves was observed for most of the soils studied here, and this will be considered later.

The distillations of soil samples after one pore volume had passed through the column show that the bottom section of the column contains about 7 percent nonconducting pores (pores that have not exchanged with the tritium tracer.) The percent nonconducting pores increases gradually up the column until the top section, which contains about 50 percent, substantially more nonconducting pores that had not exchanged with the tracing solution. Actually after one pore volume total displacement, each soil section sampled had six pore volumes pass through it, if we for the moment define a pore volume as equal to the volume of a distilled section. Section 1 has had five pore volumes of saturating fluid but only one pore of displacing fluid containing tracer pass through; section 2 has had four pore volumes of saturating fluid and two pore volumes of displacing fluid pass through, etc. Section 1 of runs 1 and 2, which has had only one pore volume of displacing fluid pass through it, has a distillation value of approximately 50 percent. This corresponds to $C/C_o = 0.5$ at one pore volume on the breakthrough curve. This point indicates that only half the pore space has been displaced after one pore volume of displacing fluid has passed through.

After two pore volume total displacements the distillations show that nonconducting pores in this soil are uniformly distributed throughout the column and are of the same magnitude as the bottom sections of the one pore volume displacements. Three pore volume total displacements show approximately the same amount of noncon-

ducting pores as two pore volume ones. It is noticed that six rather than four sections were distilled here. This was the first soil studied and the procedures and analysis were still under development. The decision to use six sections was arbitrary, and after analyzing the data the variation between sections was found to be small. It was then decided that meaningful results could be obtained with only four sections and would require less distillations. After this change in procedure was made, the only exception was when horizontal columns were used. Five sections instead of four were used here because column was constructed from five sections.

A horizontal displacement of three pore volumes was made to determine the effect of gravity in tritium tracer displacement in vertical columns. The results obtained were poor. The slope of the breakthrough, shown in Figure 8, starts to rise sharply at 0.65 pore volume up to about 0.9 pore volume, and then tails off until at about 2.5 pore volume, where $C/C_o = 1.0$. The curve is shifted about 0.13 pore volume to the left of $C/C_o = 0.5$ at one pore volume. The initial part of the curve rises at a slope of 4 to 1, indicating little mixing between the displaced and the displacing fluid. However the left shift of the breakthrough curve indicates that part of the flow occurred through channels, probably along the soil-soil column interface, and the tailing off in the latter part of the curve shows that nonequilibrium resulted. Equilibrium was established before the displacement was completed, and the distillations show that no nonconducting pores were present. The horizontal velocity was about 1.7 cm/hr (0.1$^c$ cm/sec slower than the vertical velocity), and the bulk density was 1.47 g/cm$^3$

(.12 g/cm$^3$ greater than the vertical bulk density.) Because of differences in conditions of bulk density, velocity and flow patterns, comparisons between vertical and horizontal displacement are not possible. Apparently these differences may account for the differences in the nonconducting pore volume. However because of the poor results for the horizontal displacement, no definite conclusion can be drawn about the effect of gravity on dispersion and mixing of tracer.

## Soil No. 2

### Buxton Aggregated Clay Loam

An aggregated clay loam was investigated next. It was expected that by using an aggregated soil the amount of nonconducting pores would be greater than in nonaggregated soils. This is because aggregates contain a bimodal pore size distribution. It seemed reasonable to expect that flow would occur primarily in the large pores between aggregates and that the water within the aggregates would tend to be nonconducting.

Nine columns with this soil were studied. One and three pore volume displacements at two different velocities were attempted. In some cases water was the fluid to be displaced and tritiated water was used as the displacing fluid, and in others the roles of these fluids were reversed. Changing the head, by changing the height of the reservoir, was not successful in giving constantly different flow velocities. Thirteen and three centimeter heads were used, and there was no noticeable difference in the velocities

at the different heads, Table 6. In fact, there was as much variation between velocities at the same heads as there was between velocities at different heads. However velocities during a particular measurement were fairly constant. A possible explanation is that aggregates broke down during saturation of the sample or during initial hydraulic conductivity measurements, and the amount of breakdown of the aggregates varied between columns. The velocities varied between 1.5 cm/hr and 5.5 cm/hr.

The breakthrough curves are shown in Figure 9 and the distillation data in Table 6. The breakthrough curves for the columns with the 13 cm head indicate the presence of channeling along the soil-soil column wall by their shift to the left of the $C/C_o = 0.5$ at one pore volume. The column which was first saturated with water and displaced with tritium shows the largest shift. Only one pore volume displacement at the 13 cm head was made because of this problem. From the distillations of these columns data for sections 3 and 4 show that more exclusion was apparent in the water saturated column than in the tritium saturated one, and the percent of nonconducting pores was slightly greater. The breakthrough curves for the 13 cm head start rising at about 0.3 pore volume and rise at a slope of 1.2 to 1 up to one pore volume, where the test ended.

The breakthrough curves with the 3 cm head are shown to be shifted to the right of $C/C_o = 0.5$ at one pore volume for the water saturated column, and slightly to the left of this point for the tritium saturated column. The slope of these curves is

FIGURE 9

BREAKTHROUGH CURVES FOR AGGREGATED CLAY LOAM

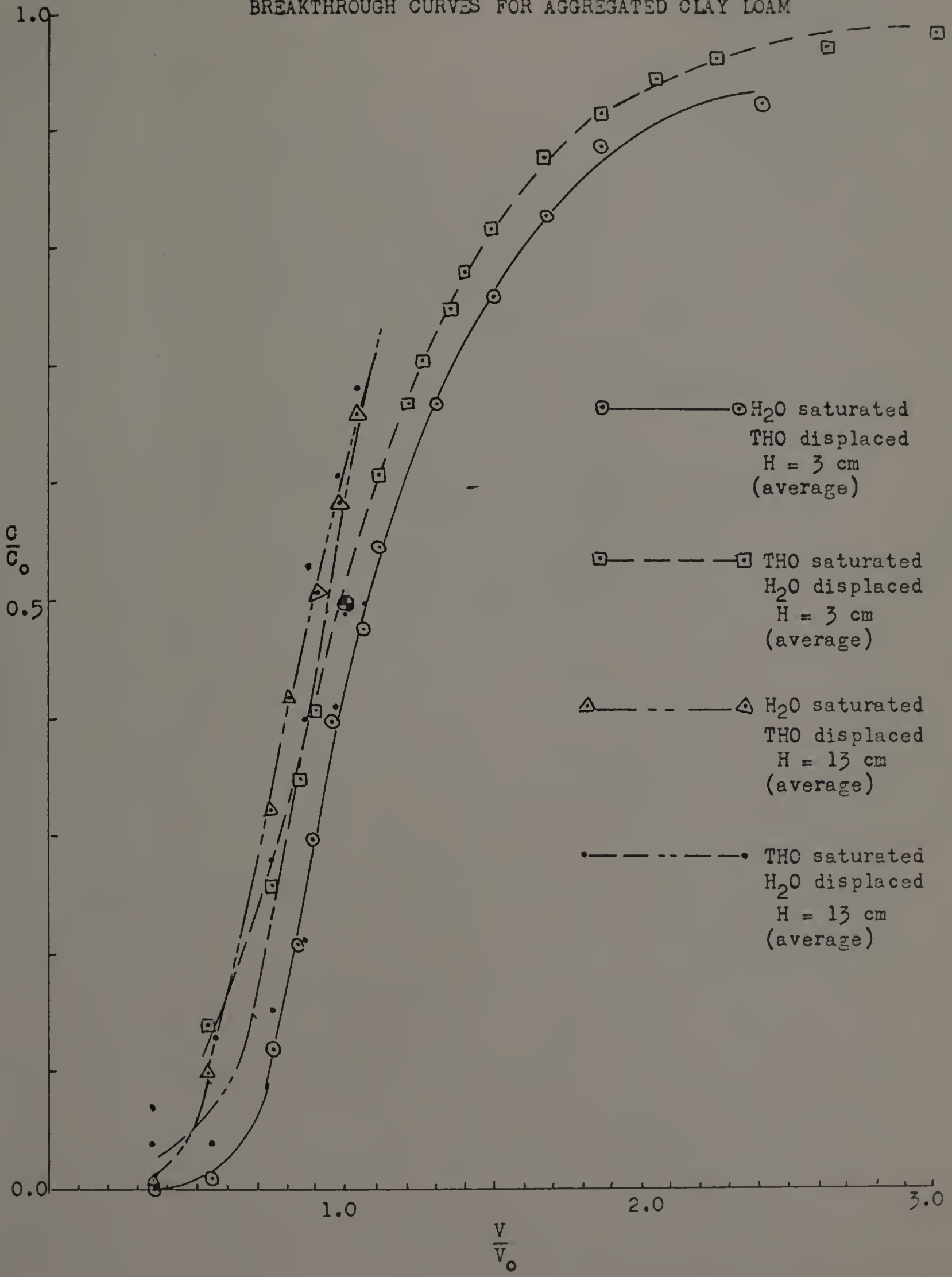


TABLE 6

EFFECT OF TWO DIFFERENT PORE VOLUME DISPLACEMENTS, TWO DIFFERENT VELOCITY HEADS AND USING TRITIATED WATER AND DISTILLED WATER AS BOTH DISPLACING AND DISPLACED SOLUTIONS, ON THE PERCENT NONCONDUCTING PORES IN BUXTON AGGREGATED CLAY LOAM

| Run | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Pore volume displaced | 1 | 1 | 1 | 1 | 1 | 3 | 1 | 3 | 3 |
| Displaced - displacing solution | $H_2O$-THO | $H_2O$-THO | THO-$H_2O$ | THO-$H_2O$ | THO-$H_2O$ | THO-$H_2O$ | THO-$H_2O$ | $H_2O$-THO | $H_2O$-THO |
| Bulk density g/cc | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 | 1.07 |
| Head $\Delta H$ cm | 13 | 13 | 13 | 13 | 3 | 3 | 3 | 3 | 3 |
| Velocity cm/hr | 4.04 | 3.17 | 2.57 | 3.20 | 1.66 | 5.30 | 3.06 | 4.00 | 1.73 |
| Section No. | Percent Nonconducting Pores | | | | | | | | |
| 1 | 44.0 | 64.0 | 55.0 | 43.0 | 34.5 | 1.2 | 51.6 | 4.1 | 2.9 |
| 2 | 60.0 | 46.0 | 4.8 | 4.1 | 3.5 | 0.7 | 15.1 | 4.0 | 2.0 |
| 3 | 10.0 | 2.0 | 1.4 | 1.4 | 1.2 | 0.7 | 1.2 | 5.9 | 4.0 |
| 4 | 8.0 | 3.0 | 1.5 | 0.9 | 0.9 | 0.6 | 0.9 | 2.0 | 1.6 |

also 1.2 to 1. The slopes of these curves indicate that some mixing is occurring during breakthrough, more so than was present with the unidentified sandy loam. Breakthrough starts around 0.35 pore volume, rises to about $C/C_o$ = 0.6 and 1.2 pore volume and then tails off at the end. Nonequilibrium conditions were not observed with the 13 cm head because only one pore volume was displaced. However, because of exclusion, this condition is certain to have existed. Because three pore volumes were run at the 3 cm head this nonequilibrium is seen to be marked. More tailing off appears to be present in the water saturated column than the tritium saturated column. This is supported by the distillation data, which shows slightly more nonconducting pores for the water saturated column. If a correction could be applied for gravity effects on the columns run at 3 cm head, it is expected that the water saturated column would still remain shifted to the right of $C/C_o$ = 0.5 at one pore volume but would come closer to this point, and the tritium saturated curve would be shifted from the left to the right of this point and the two would fall very close to one another.

The distillations of the column which underwent one pore volume total displacement show a small percentage of nonconducting pores in the bottom two sections and more in the upper two. After one pore volume total displacement, each soil section has had four pore volumes pass through it, defining a pore volume for the moment as equal to the void volume of a distilled section.

Section 1 has had three pore volumes of saturating fluid and one pore volume of displacing fluid pass through; section 2 has had two pore volumes of saturating fluid and two pore volumes of displacing fluid pass through, etc. Section 1 of runs 1 and 2, which has had only one pore volume of displacing fluid pass through it, has a distillation value of approximately 50 percent. This corresponds to $C/C_o = 0.5$ at one pore volume on the breakthrough curve. This point indicates that only half the pore space has been displaced after one pore volume of displacing fluid has passed through.

After three pore volumes have passed through the column, the amount of nonconducting pores is evenly distributed the length of the column. Despite variation in amount between columns, it is about 2 or 3 percent. Velocity through the columns appears to have little effect on the amount present. The reason for more nonconducting pores being found when water is used to saturate the column rather than tritium is uncertain, unless the effect of gravity tends to keep the tritium in the column and tritium thus dilutes the displacing water.

From these results it appears that there are few nonconducting pores in this aggregated clay loam. However, because of the uncertainty of the stability of the aggregate, it was decided to test another aggregate later, preferably a stable one, and compare them.

## Soil No. 3

### Hadley Fine Sandy Loam

A different textured sandy loam was used to see effects of texture on percent nonconducting pores. The breakthrough curves for Hadley fine sandy loam are shown in Figure 10, and the distillation data in Table 7. Three pore volume displacements were performed on two columns initially saturated with water and also on one column initially saturated with tritiated water. Also a 1.5 pore volume displacement was made on a column initially saturated with water. These columns were displaced at an average velocity of 0.42 cm/hr. All the breakthrough curves are shifted to the right of the point $C/C_o = 0.5$ at one pore volume. More mixing appears to have occurred in the column initially saturated with tritium than in those which were water saturated. The tritium saturated breakthrough curve starts at 0.25 pore volume and rises at a slope of 0.9 to 1. At $C/C_o = 0.80$ the curve flattens slightly and reaches $C/C_o = 1$ at 1.9 pore volume.

The breakthrough curves for the water saturated columns are similar in shape to each other, but 1.5 pore volume curve breaks through 0.1 of a pore volume earlier than the 3 pore volume curve. The 1.5 pore volume displacement starts at 0.60 pore volume and rises at a slope of 2 to 1. Because only 1.5 pore volume was collected, the curve does not reach $C/C_o = 1.0$. The water saturated three pore volume displacement starts at 0.70 pore volume and rises at a slope of 2 to 1. The curve flattens slightly at

FIGURE 10

BREAKTHROUGH CURVES FOR HADLEY SANDY LOAM

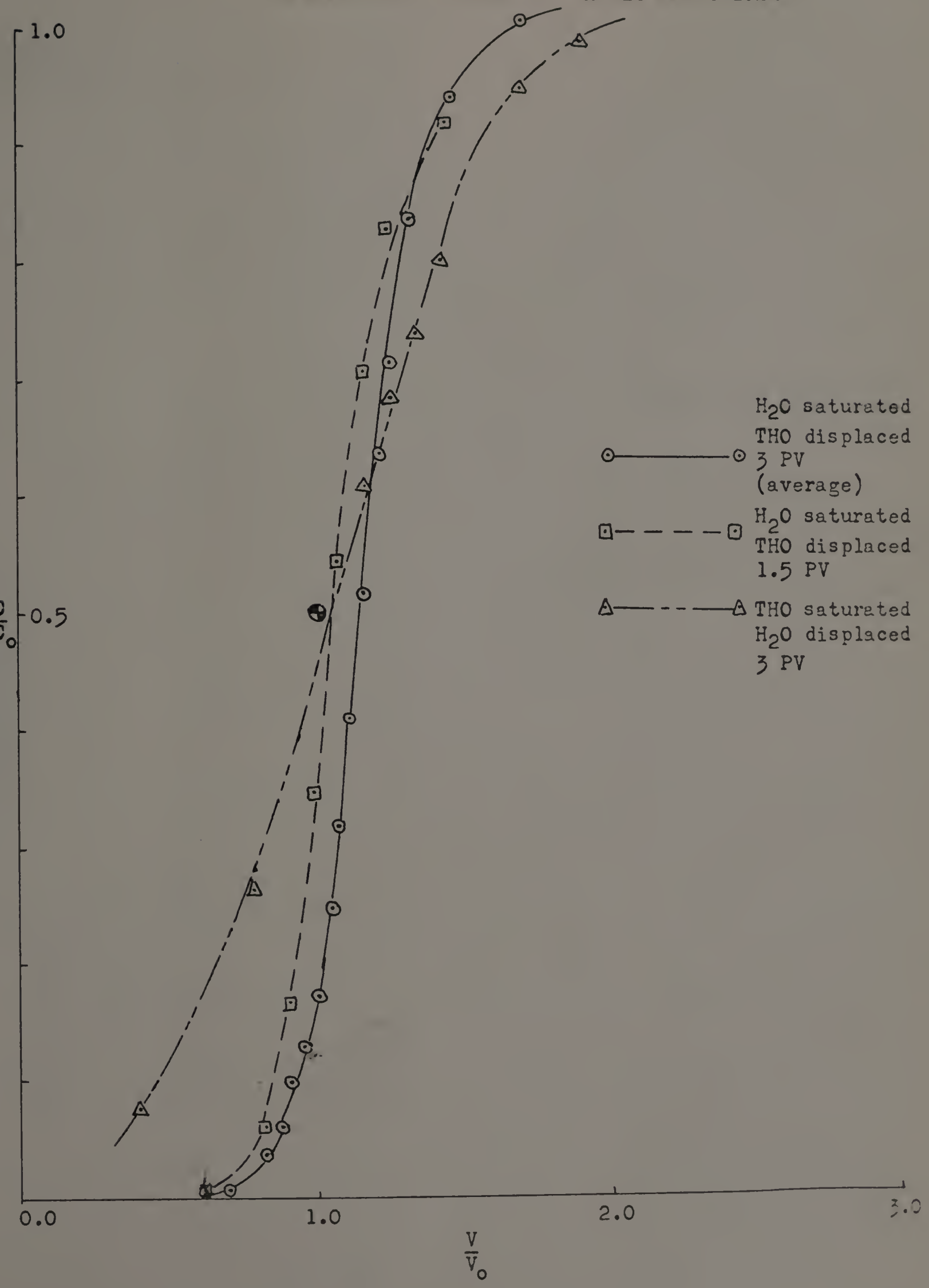


TABLE 7

EFFECT OF TWO DIFFERENT PORE VOLUME DISPLACEMENTS AND OF USING TRITIATED WATER AND DISTILLED WATER AS BOTH DISPLACING AND DISPLACED SOLUTIONS ON THE PERCENT NONCONDUCTING PORES IN HADLEY FINE SANDY LOAM RUN AT A 13 CM HEAD

| Run | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Pore volume displaced | 3.0 | 1.5 | 3.0 | 3.0 |
| Displaced - displacing solution | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | THO-$H_2O$ |
| Bulk density | 1.31 | 1.31 | 1.31 | 1.31 |
| Head $\Delta H$ cm | 13 | 13 | 13 | 13 |
| Velocity cm/hr | .48 | .40 | .36 | .46 |
| Section No. | Percent Nonconducting Pores | | | |
| 1 | 2.0 | - | 1.5 | 0.6 |
| 2 | 2.1 | 4.0 | 1.2 | 0.6 |
| 3 | 2.0 | 3.0 | 1.1 | 0.6 |
| 4 | 1.9 | 2.0 | 1.1 | 0.6 |

$C/C_o$ = .80 and continues until reaching $C/C_o$ = 1.0 at 1.70 pore volume.

The distillation data shows that after three pore volume the nonconducting pores are uniformly distributed the length of the column. The water saturated columns contain about 1.5 percent nonconducting pores, while the tritium saturated column shows only 0.6 percent. This seems to agree with the breakthrough curves, which show that more mixing occurred in the tritium saturated column than in the water saturated ones.

After 1.5 pore volumes have passed through the column, a slight variation in nonconducting pores between the top and the bottom of the column could indicate that equilibrium has not quite been established. However this variation is no greater than variations found for other distillation data within a column.

The results suggest there is about 1.5 percent nonconducting pores for tritiated water displacing distilled water, and about .6 percent for distilled water displacing tritiated water.

## Soil No. 4

## Windsor Loamy Sand

A coarse sandy loam soil was investigated next. This soil was used to determine the effect of a coarse textured soil on percent nonconducting pores.

Three and five pore volume displacements at two different velocity heads were tried. The soil columns were all initially saturated with water and then displaced with tritiated water.

Four of the soil columns were displaced vertically at a 3 cm head, one soil column was displaced horizontally at a 3 cm head, and one soil column was displaced vertically at a 15 cm head. The breakthrough curves are shown in Figure 11 and the distillation data in Table 8. The results of these tests were poor. All the breakthrough curves are shifted to the left of $C/C_o$ = 0.5 at one pore volume, indicating exclusion. The tailing off at the end of the breakthrough curve shows that nonequilibrium conditions existed in the columns. Apparently most of the flow occurred up the sides of the column or through channels that developed, and this is supported by the distillation data, which shows large fluctuation in the percent nonconducting pores in the various sections.

This is one of the useful aspects of the distillation technique because the column itself can be examined to determine the tritium distributions and, in turn, the flow patterns in the column. In this case the flow up the sides of the column, which is shown as exclusion on the breakthrough curve, is verified by the irregular distribution of tritium in the sampled sections of the column.

Three or five pore volume displacements apparently had no effect. Breakthrough for the curves occurs almost immediately for all the curves. The vertical columns run at 3 cm heads show the most exclusion, and the horizontal column which was run at a 3 cm head shows the least amount of exclusion. The horizontal displacement was made to determine the effect of gravity, but because of poor data was inconclusive.

FIGURE 11

BREAKTHROUGH CURVES FOR WINDSOR LOAMY SAND

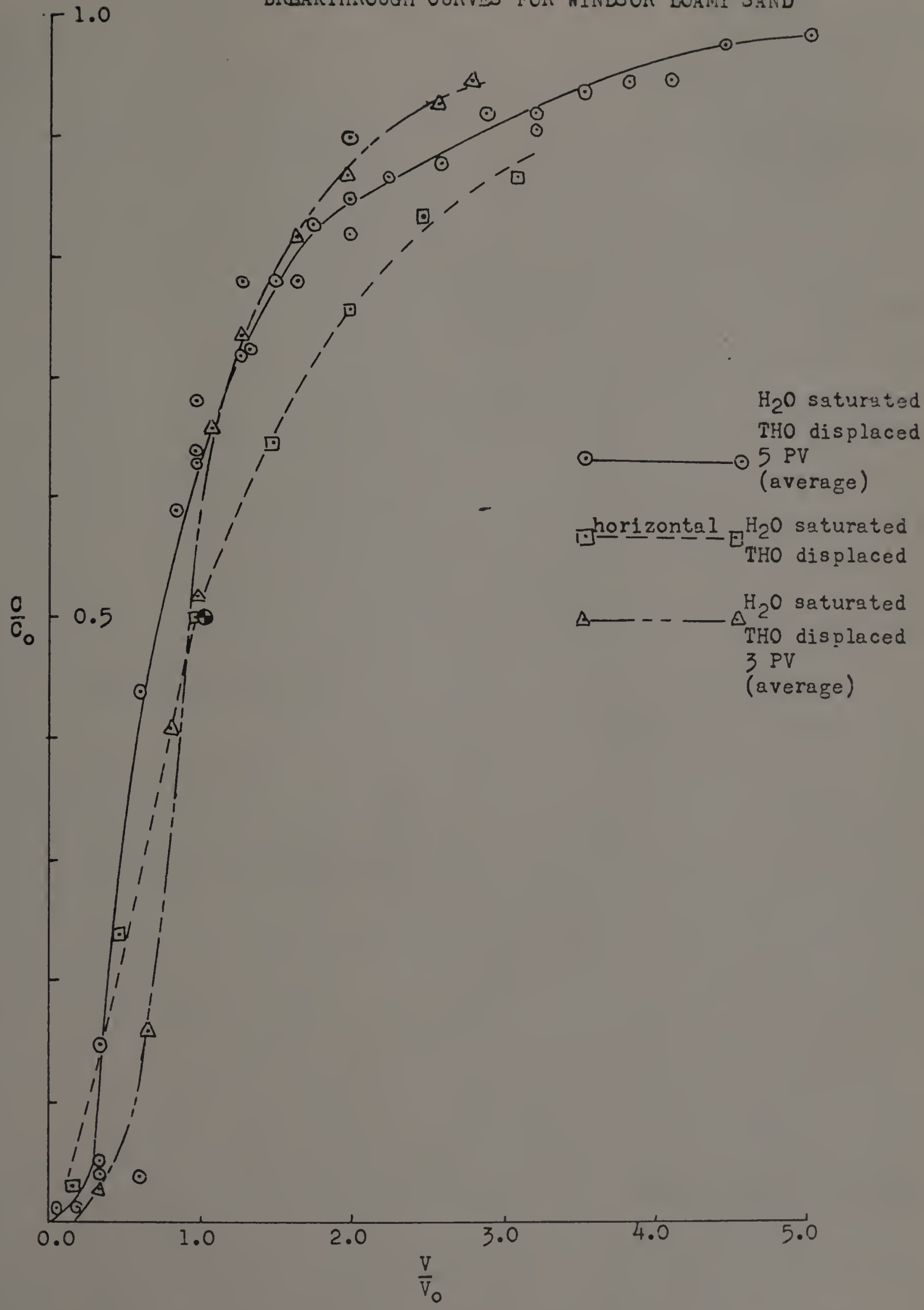


TABLE 8

EFFECT OF TWO DIFFERENT PORE VOLUME DISPLACEMENTS, TWO DIFFERENT HEADS, AND COLUMN ORIENTATION, ON THE PERCENT NONCONDUCTING PORES IN WINDSOR LOAMY SAND WHEN DISPLACING DISTILLED WATER WITH TRITIATED WATER

| Run | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Pore volume displaced | 3 (vertical) | 3 (vertical) | 5 (vertical) | 5 (vertical) | 3 (vertical) | 3 (horizontal) |
| Displaced - displacing solution | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO | $H_2O$-THO |
| Soil Density | 1.73 | 1.73 | 1.73 | 1.73 | 1.73 | 1.63 |
| Head $\Delta H$ cm | 15 | 3 | 3 | 3 | 3 | 3 |
| Velocity cm/hr | 13.1 | 7.81 | 7.71 | 10.11 | 10.33 | 5.38 |
| Section No. | Percent Nonconducting Pores | | | | | |
| 1 | 55.0 | 57.0 | | 37.0 | 64.0 | 15.0 |
| 2 | 13.0 | 34.0 | 30.0 | 31.0 | 70.0 | 10.0 |
| 3 | 3.0 | 50.0 | 22.0 | 27.0 | 38.0 | 6.0 |
| 4 | 3.0 | 1.0 | 0.0 | 2.5 | 31.0 | 9.0 |
| 5 | | | | | | 1.0 |

No meaningful results about the influence of soil texture on nonconducting pores were obtained for this soil because of the difficulties with the experimental setup, but it is likely the amount of nonconducting pores for this soil would be about one percent, based on what was obtained for the other soils and also on the grain size analysis for this soil.

## Soil No. 5

## Ottawa Sand

Because of the literature review, the results which were obtained thus far were somewhat unexpected in that higher values of nonconducting pores were originally anticipated. Therefore it was decided to use Ottawa sand and compare the results for this sand with the other soils used in this study. Ottawa sand was chosen because it is a coarse, poorly graded sand and because of this would be expected to contain very little nonconducting pores when compared with the other soils used. Also data exists for this sand from other investigations. Coates and Smith (9) arrived at a value for stagnant pore volume of 5 percent for Ottawa sand. Rose and Passioura (38) in repeating Coates and Smith's work, came to the conclusion that the value of the stagnant volume for Ottawa sand should be less than 5 percent. The results from Ottawa sand from the present study can be compared to these results.

The breakthrough curve for Ottawa sand is shown in Figure 12, and the distillation data in Table 9. Three pore volume displacements and an average velocity of about 55 cm/hr were used. Two

FIGURE 12

BREAKTHROUGH CURVES FOR OTTAWA SAND

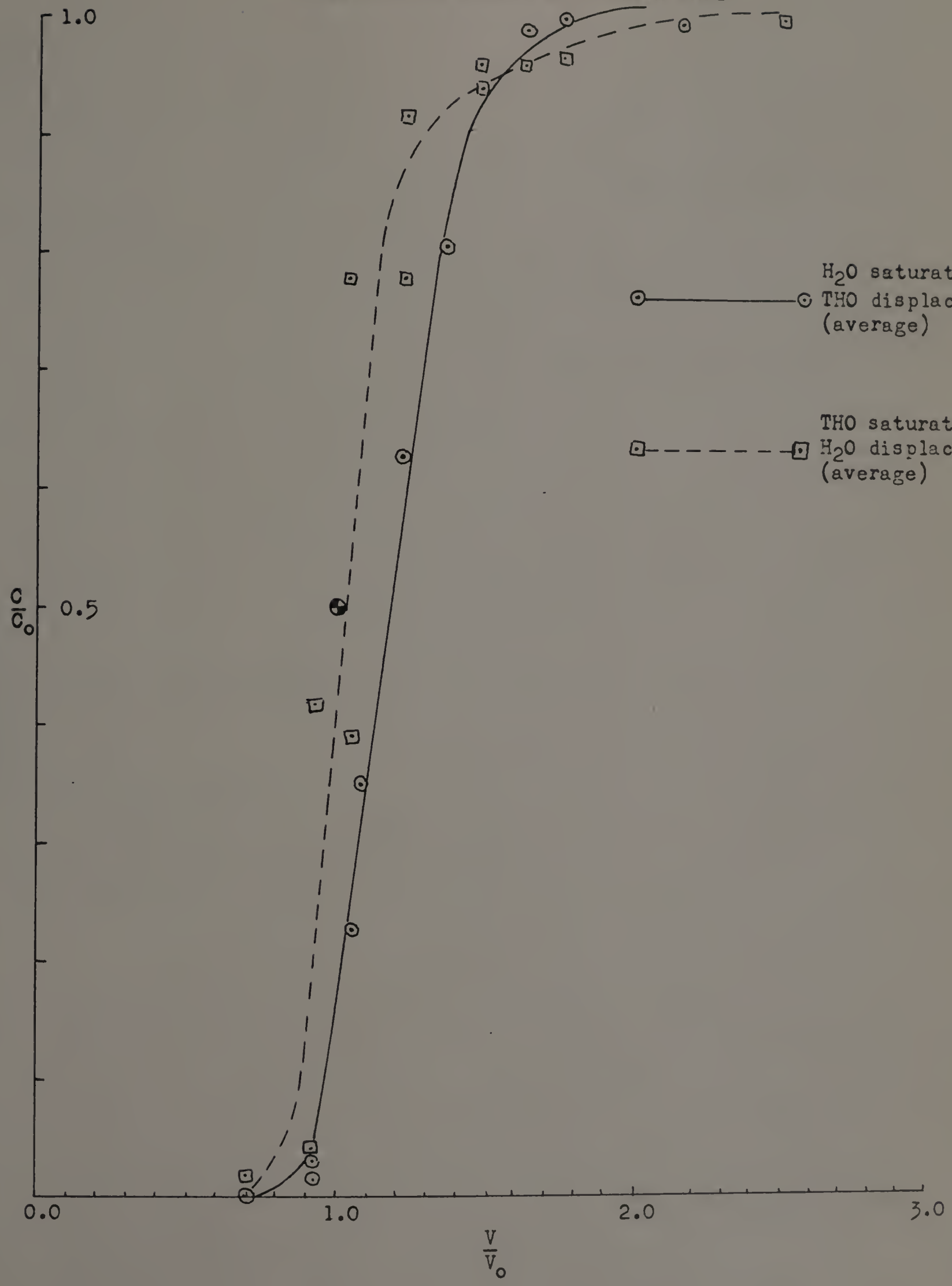


TABLE 9

EFFECT OF TRITIATED WATER AND WATER AS BOTH DISPLACED AND DISPLACING SOLUTIONS ON THE PERCENT NONCONDUCTING PORES IN OTTAWA SAND DISPLACED AT A 3 CM VELOCITY HEAD WITH 3 PORE VOLUMES

| Run | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Pore volumes displaced | 3 | 3 | 3 | 3 |
| Displaced - displacing solution | $H_2O$-THO | THO-$H_2O$ | THO-$H_2O$ | $H_2O$-THO |
| Bulk density | 1.84 | 1.84 | 1.84 | 1.84 |
| Head $\Delta H$ cm | 3 | 3 | 3 | 3 |
| Velocity cm/hr | 48.10 | 55.52 | 64.32 | 45.01 |
| Section No. | Percent Nonconducting Pores | | | |
| 1 | 1.0 | 1.3 | 0.9 | 2.1 |
| 2 | 3.0 | 0.9 | 0.8 | 9.0 |
| 3 | 2.0 | 0.8 | 0.8 | 1.9 |
| 4 | 4.0 | 1.0 | 0.8 | 2.0 |

columns were saturated with water and displaced with tritiated water, and two columns were saturated with tritiated water and displaced with water. The breakthrough curves for the water saturated and tritium saturated columns are shifted to the right of $C/C_o = 0.5$ at one pore volume. The curves for the water saturated column is shifted further to the right than curves for the tritium saturated columns. The curves start to rise at 0.7 pore volume at a slope of 3 to 1. This steep slope indicates little mixing occurred between the displaced and displacing fluid. There is more, however, than in the unidentified sandy loam but less than in the other soils. The curves become flatter when the curves reach 0.9 pore volume.

The distillation data shows that after three pore volumes have been displaced, the percent nonconducting pores are fairly uniformly distributed throughout the column and comprise about 2.5 percent for water displaced by tritium, and about 1.0 percent for tritium displaced with water of the void volume. These results agree more closely with the results of Rose and Passioura than with Coates and Smith.

These results appear significant in light of the results obtained for the other soils. A very coarse sand, poorly graded, run at a high flow velocity, contains about 1 to 2 percent nonconducting pores, which is essentially the same that is found in fairly well graded soils with a wide range in pore size distribution. The bulk densities and the velocities for these soils are not the

same as for the Ottawa sand, which may account for some of the unexpected results.

## Soil No. 6

### Heated Montmorillonite

Because of the instability of the previously run aggregated clay loam, an aggregated, sodium saturated montmorillonite was heated to 700° C, which formed a stable aggregate that would not break down during displacement, and was tested. Three vertical and one horizontal columns at a 3 centimeter velocity head were displaced with three pore volumes. One of the vertical columns and the horizontal column were saturated with water and displaced with tritiated water. The other two vertical ones were saturated with tritiated water and displaced with water. The flow velocities through the vertical columns averaged about 25 cm/hr and through the horizontal one 15 cm/hr. The bulk density for all the columns was the same. The breakthrough curves are shown in Figure 13 and the distillation data in Table 10.

There was some concern that, due to the relatively high velocity and the coarseness of the aggregate (Table 2), flow would occur by channeling up the sides of the column and not through the porous media. The column sampling procedure was therefore modified by distilling the center portion of each section separate from the outer portion. Center portions were obtained with a cork borer. The number of sections remained the same except for the horizontal column when five sections were sampled. In

Table 10 each section shows two distillation values. The first value, labeled center, is the percent nonconducting pores for the center of the particular section, and the second value, labeled outer, is the percent nonconducting pores for the outer portion of the same section. Comparing the results of the central and outer portions of each section, it appears that flow occurred through the porous media as it should and not through channeling. This is also evident from the position and shape of the breakthrough curves.

The breakthrough curves are shifted to the right of $C/C_o = 0.5$ at one pore volume. The water saturated vertical column is shifted further right of this point than the tritium saturated ones. The breakthrough of the water saturated column starts at 0.45 pore volume and rises at a slope of 0.8 to 1 until it reaches $C/C_o = 0.8$ at 1.5 pore volume, where it flattens slightly and reaches $C/C_o = 1$ at 2.5 pore volumes. The tritium saturated column starts at 0.38 pore volumes, rising at a slope of 0.8 to 1 until $C/C_o = 0.8$ at 1.4 pore volume and then flattens slightly until it reaches $C/C_o = 1.0$ at 1.80 pore volume.

The breakthrough curve for the horizontal column starts at 0.55 pore volume, rising at a slope of 1 on 1 and reaches $C/C_o = 1.0$ at 1.87 pore volume. Less mixing appears to have occurred in the horizontal column than in the vertical ones, as seen from the slope of the breakthrough curve.

There appears to be a definite difference in percent nonconducting pores between the horizontal and vertical columns. Vertical columns contained about 2 to 3 percent for the water

FIGURE 13

BREAKTHROUGH CURVES FOR HEATED MONTMORILLONITE

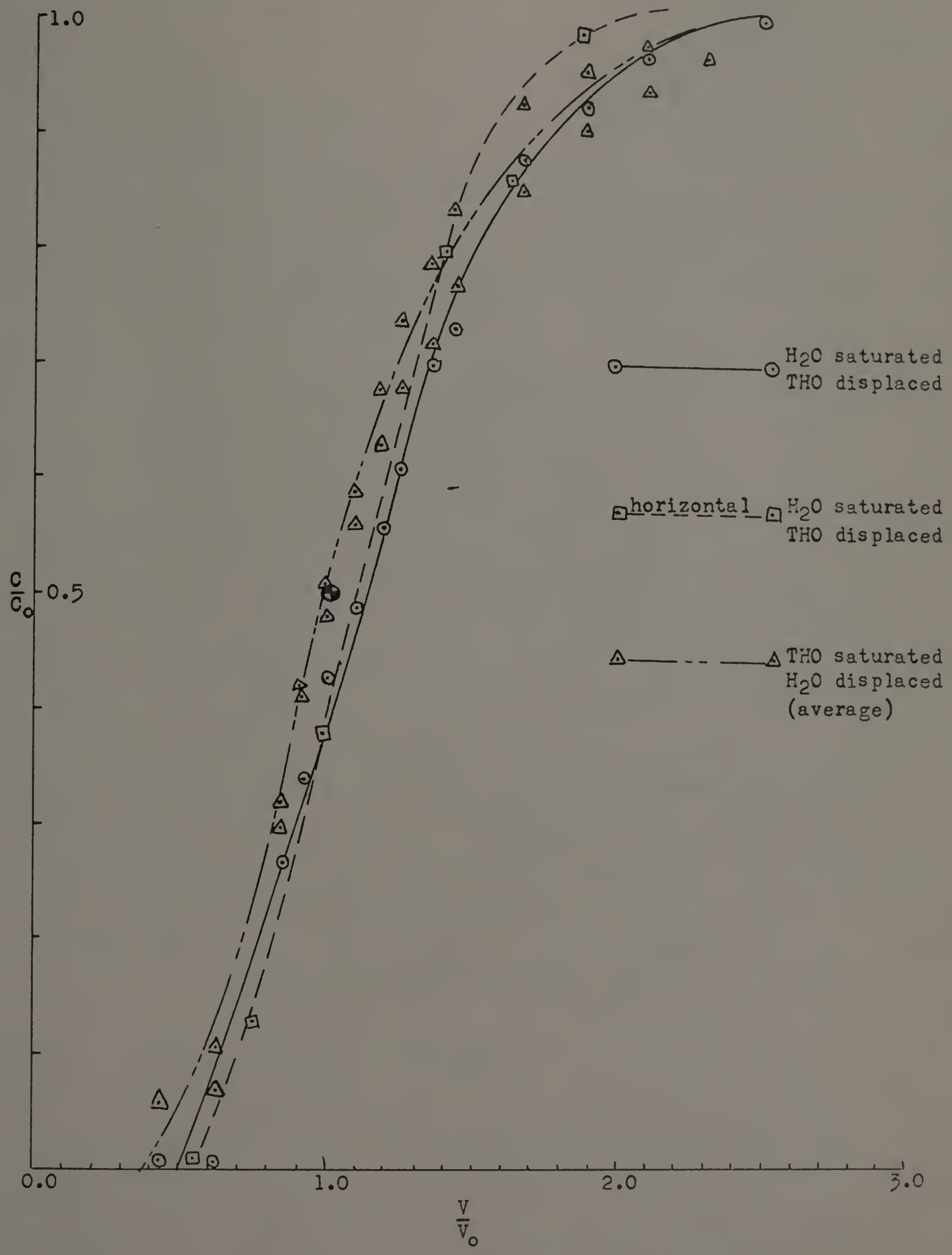


TABLE NO. 10

EFFECT OF USING TRITIATED WATER AND DISTILLED WATER AS BOTH DISPLACING AND DISPLACED SOLUTION, AND COLUMN ORIENTATION ON THE PERCENT NONCONDUCTING PORES IN PREHEATED MONTMORILLONITE AGGREGATE RUN AT A 3 CM HEAD WITH 3 PORE VOLUME DISPLACEMENTS

| Run | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Pore volumes displaced | 3 (vertical) | 3 (vertical) | 3 (vertical) | 3 (horizontal) |
| Displaced - displacing solution | $H_2O$-THO | THO-$H_2O$ | THO-$H_2O$ | $H_2O$-THO |
| Bulk density g/cc | 1.24 | 1.24 | 1.24 | 1.24 |
| Head $\Delta H$ cm | 3 | 3 | 3 | 3 |
| Velocity cm/hr | 22.16 | 22.09 | 30.01 | 14.84 |
| Section No.* | Percent Nonconducting Pores | | | |
| 1. Center | 4.0 | 2.0 | 1.7 | 9.2 |
| Outer | 2.1 | 2.2 | 1.6 | 16.0 |
| 2. Center | 3.0 | 1.6 | 1.5 | 8.8 |
| Outer | 2.0 | 1.5 | 1.3 | 8.9 |
| 3. Center | - | 1.5 | 1.3 | 9.5 |
| Outer | 2.0 | 1.7 | 1.0 | 8.7 |
| 4. Center | - | 1.3 | 1.3 | 10.1 |
| Outer | 2.0 | 1.2 | 1.0 | 7.1 |
| 5. Center | | | | 7.6 |
| Outer | | | | 7.7 |

*Refer to pages 60 and 61.

saturated, tritiated water displaced column, and 1.5 percent for the tritiated water saturated, water displaced column, while the horizontal contain about 9 percent. Since only one horizontal displacement was made, more would be necessary to verify this.

## Displacement and Distillation

It is of interest to discuss the effect of the vertical column on the displacements and the distillations. The breakthrough curves were used primarily to determine if anything unusual was occurring in the system, such as exclusion, which may affect the results of the distillations. The distillations were of primary interest but the breakthrough curves show certain characteristics which may have had an effect on the distillation.

In most cases the position of the breakthrough curve was shifted to the right of $C/C_o = 0.5$ at one pore volume. In a few cases the shift was over 0.1 pore volume. Another aspect of the breakthrough curves was that in all cases the breakthrough curves for the columns saturated with tritiated water appeared to the left of the breakthrough curves for the columns saturated with water. The author believes that these two characteristics are the result of gravity affecting the vertical displacements.

Several aspects of miscible displacement can cause this shifting of the curves to the right of $C/C_o = 0.5$ at one pore volume. These include gravity, dilution, improper accounting for the quench of tritium counts, and a loss of tritium by exchange, isotopic fractionation and enhanced reaction kenetics. Several of these have been mentioned before and are worthy of further consideration.

Quench correction is important in a study of this type. Quenching is caused by dissolved materials and suspended particles in the counting solution of the tritium samples. Calibration

curves, prepared from samples which had been deliberately quenched, were used to correct for quenching of the count rates by the external standard ratio method. Distillation samples were not corrected for quench because quenching was negligible. Without quench corrections for the displacement samples, the count rate is lower and this results in a shifting of the breakthrough curve to the right. It was noted, however, that in samples with excessive quench, even after correction the values of the concentration ratios seemed low. Only after distilling the samples did the values look reasonable. Distillation of all breakthrough samples to eliminate quench would be impractical, but this points to the reliability of the quench corrections. The corrections work very well when there is only a small amount of quench or when excessively quenched samples have an activity around background. But for high quenching of high activity samples, quench corrections appeared to be insufficient. This, in turn, affects the position of the breakthrough curve and the amount of shifting depends on the amount of uncorrected quenching.

Exchange between the tritiated water molecule and crystal lattice hydroxyls could possibly account for shifting the breakthrough curve to the right. A mass balance of tritium was worked out for breakthrough and distillation data. The amount of tritium which could be accounted for by exchange with hydroxyls was a fraction of a percent, which would be negligible in its effect on the position of breakthrough curves and distillation data.

From a consideration of these points it appears that only a portion of the shift in the breakthrough curves can be accounted for by considerations other than gravity.

The amount of shift caused by gravity was investigated by comparing vertical and horizontal displacements. Displacements in three of the materials were made, using the same heads and similar bulk densities to those in the vertical columns. The bulk densities could not be matched exactly. The soils used were the unidentified sandy loam, Windsor loamy sand, and the aggregated montmorillonite. The sandy loam and loamy sand soils showed exclusion effects due to channeling along the sides of the column. The montmorillonite breakthrough curves appeared to be reasonable in that the curve lies to the right of $C/C_o = 0.5$ at one pore volume. Depending on how smoothly the data points are connected on the graph, it is seen that gravity may be expected to cause a 5 percent shift to the right of the horizontal breakthrough curve. The difference in breakthrough curves obtained when tritiated water and distilled water are displaced also suggests this. It might be considered that this difference may be explained by a tendency for tritium to be adsorbed more tenaciously than protium. However, unpublished work performed by Stewart* on tritium interaction with clay minerals suggests that although there is a slight

---

*Personal communication with Dr. G. L. Stewart, Prof. of Soil Physics, Dept. of Plant and Soil Sciences, Univ. of Mass., Amherst, Mass.

tendency for tritium to be adsorbed more tenaciously than protium, this effect would be negligible and would not account for differences observed in the present study.

It appears, therefore, that gravity has an effect in the breakthrough curve. The gravity effect arises because the mass of the tritiated water molecule is greater than the water molecule, and therefore there is a tendency for the tritiated molecule to preferentially remain in the column.

If this is the case, then it might be expected that the distillation would show a gravity effect. The data for the montmorillonite is again of interest. It is emphasized that only one horizontal displacement was made, and more are necessary to verify the results. The horizontal column shows about 9 percent nonconducting pores and the vertical columns about 1.5 percent. It might be argued that because dispersion increases with velocity, the higher velocities would result in fewer nonconducting pores. Looking at the velocity and the percent nonconducting pores for the different runs, this does not appear to hold. A possible reason is that the dispersion increases due to greater velocities in the conducting pores, and the nonconducting pores are not affected by change in amount of dispersion due to changing velocity. It seems reasonable to expect that at least part of the difference in nonconducting pores between vertical and horizontal columns is accounted for by gravity.

# SUMMARY

From the tables showing nonconducting pores for the different soils it is apparent that in disturbed soils, coarse sand and aggregated montmorillonite the percent nonconducting pores is small and there is no noticeable difference between the different textured materials. The velocities used in this study were relatively high but the effect of velocity in the columns appeared to have little effect on percent nonconducting pores. The amount was influenced more by the number of pore volumes which passed through the column, up to about 1.5 pore volumes. Equilibrium was noticed to be fairly well established when between one and two pore volumes had been displaced.

Although the percent nonconducting pores is small there is a difference, depending on which solution (tritiated water or distilled water) is being displaced and which is displacing. The columns where tritiated water is being displaced by distilled water consistently show less nonconducting pores than when distilled water is being displaced by tritiated water. This suggests that gravity may be influencing the results, since the tritiated water molecule tends to remain in the column.

It was seen in this study that the use of tritiated water as a tracer was useful in analyzing the breakthrough curves. After the displacements have been made, the column itself may be investigated and give additional information about flow as well

as support information given by the breakthrough curves. For example, exclusion due to channeling up the sides of the column resulted in the breakthrough curve shifting to left of $C/C_o = 0.5$ at one pore volume, and distillations show erratic large percentage of nonconducting pores.

As mentioned before, convection, diffusion and chemical reaction are the components which make up dispersion. Exchange of tritium with hydroxyls is negligible, so that convection and diffusion are the major components. Since these cannot be separated in the flow system, the importance of pores which are primarily involved in the net transport of water (due primarily to convection) would be underestimated due to diffusion of tracer into the less important pores which do not contribute much to the net transport.

By performing a mass balance on the displacements and distillations obtained here it is possible to account for all but one percent of the tritium which passed through or remained in the system. From these mass balances and equilibrium calculations the amount of tritium lost by exchange with hydroxyls was found to be insignificant. One interesting observation in performing the mass balance was the importance of knowing the exact volume of effluent which was collected by the fractionator during displacement. Slight variations in volume can cause large discrepancies.

From the results of this study it would be interesting to perform more horizontal displacements and find out how much more,

if any, gravity affects vertical columns than horizontal ones in terms of percent nonconducting pores and in position and shape of breakthrough curves. It would also be interesting to determine if a difference is observable between tritiated water and distilled water when they are both used as displacing and displaced solutions in horizontal columns.

# LITERATURE CITED


1. Bear, J. 1972. Dynamics of Fluids in Porous Media. American Elsevier Publishing Co., Inc., New York.

2. Biggar, J. W. and D. R. Nielson. 1962. Miscible Displacement: II Behavior of Tracers. Soil Sci. Soc. Amer. Proc. Vol. 26, No. 2, 125-128.

3. Biggar, J. W. and D. R. Nielson. 1963. Miscible Displacement: V Exchange Processes. Soil Sci. Soc. Amer. Proc., Vol. 27, No. 6, 623-627.

4. Black, C. A. (ed.). 1965. Methods of Soil Analysis, Part 1, Agronomy 9. Amer. Soc. Agron., Madison, Wis.

5. Blackwell, R. J., J. R. Rayne and M. W. Terry. 1959. Factors Influencing the Efficiency of Miscible Displacement. Trans. AIME, 217, 1-8.

6. Briggs, L.J. 1897. Mechanics of Soil Moisture. USDA Bureau of Soils, Bul. No. 10, Washington Govt. Printing Office.

7. Buckingham, E. 1907. Studies on the Movement of Soil Moisture. USDA Bur. of Soils Bul. No. 38, Govt. Printing Office.

8. Burd, J. S. and J. C. Martin. 1923. Water Displacement of Soils and the Soil Solution. Jour. of Agr'l Sciences, Vol. 13, 265-295.

9. Coates, K. H. and B. D. Smith. 1964. Dead End Pore Volume and Dispersion in Porous Media. Soc. of Petroleum Engineers Jour., Vol. 4, 73-84.

10. Darcy, H. 1856. Les Fountaines Publique de la Ville de Dijou, Dalmont, Paris.

11. Day, P. R. and W. M. Forsythe. 1957. Hydrodynamic Dispersion of Solutes in the Soil Moisture Stream. Soil Sci. Soc. Amer. Proc., Vol. 21, No. 5, 477-480.

12. Deans, H. A. 1963. A Mathematical Model for Dispersion in the Direction of Flow in Porous Media. Trans. AIME, Vol. 228, 49.

13. Elrich, D. E. and L. K. French. 1966. Miscible Displacement Patterns on Disturbed and Undisturbed Soil Cores. Soil Sci. Soc. Amer. Proc., Vol. 30, No. 2, 153-156.

14. Green, R. E. and J. C. Corey. 1971. Calculation of Hydraulic Conductivity: A Further Evaluation of Some Predictive Methods. Soil Sci. Soc. Amer. Proc., Vol. 35, No. 1, 3-8.

15. Green, R. E., P. S. C. Rao and J. C. Corey. 1972. Solute Transport in Aggregated Soils: Tracer Zone Shape in Relation to Pore Velocity Distribution and Adsorption. Proc. of 2nd Symposium on Fundamentals of Transport Phenomenon in Porous Media. Guelph, Ontario, Canada. Vol. 2, 732-752.

16. Handy, L. L. 1959. An Evaluation of Diffusion Effects in Miscible Displacements. Trans. Am. Inst. Mech. Eng., Vol. 216, 61-63.

17. Hilgard, E. W. 1919. Soils. The Macmillan Company, London.

18. Kaufman, W. J. and G. T. Orlob. 1956. An Evaluation of Groundwater Tracers. Trans. Amer. Geophys. Union, Vol. 37, No. 3, 297-306.

19. Keen, B. A. 1931. The Physical Properties of the Soil. The Rothamsted Monograph on Agricultural Science, Longman, Green & Co., London, New York, Toronto, Chapter 3, 89-126.

20. King, F. H. 1907. Textbook of the Physics of Agriculture. Madison, Wis.

21. Kirkham, D. and W. L. Powers. 1972. Advanced Soil Physics. Wiley-Interscience, New York.

22. Kissel, D. E., J. T. Ritchie and E. Burnett. 1973. Chloride Movement in Undisturbed Swelling Clay Soils. Soil Sci. Soc. Amer. Proc., Vol. 37, No. 1, 21-24.

23. Krupp, H. K. and D. E. Elrich. 1968. Miscible Displacement in an Unsaturated Glass Bead Medium. Water Resources Research, Vol. 4, No. 4, 809-815.

24. Krupp, H. K. and D. E. Elrich. 1969. Density Effects in Miscible Displacement Experiments. Soil Science, Vol. 107, No. 5, 372-380.

25. Kunze, R. J., G. Uehara and K. Graham. 1968. Factors Important in the Calculation of Hydraulic Conductivity. Soil Sci. Soc. Amer. Proc., Vol. 32, No. 6, 760-765.

26. Lambe, T. W. 1951. Soil Testing for Engineers. John Wiley and Sons, Inc. New York.

27. Lapidus, L. and N. R. Amundsen. 1952. Mathematics of Adsorption in Beds IV, Jour. of Physical Chemistry, Vol. 56, 984-988.

28. Marshall, T. J. 1958. A Relation between Permeability and Size Distribution of Pores. J. Soil Sci., Vol. 9, No. 1, 1-8.

29. Millington, R. J. and J. P. Quirk. 1960. Transport in Porous Media. 7th International Congress of Soil Science, Madison, Wis., 97-106.

30. Nakayama, F. S. and R. D. Jackson. 1963. Diffusion of Tritiated Water in Soils. Soil Sci. Soc. Amer. Proc., Vol. 27, No. 3, 255-258.

31. Nielson, D. R. and J. W. Biggar. 1961. Miscible Displacement in Soils: I Experimental Information. Soil Sci. Soc. Amer. Proc., Vol. 25, No. 1, 1-5.

32. Nielson, D. R. and J. W. Biggar. 1962. Miscible Displacement: III Theoretical Considerations. Soil Sci. Soc. Amer. Proc., Vol. 26, No. 3, 216-221.

33. Nielson, D. R. and J. W. Biggar. 1963. Miscible Displacement: IV Mixing in Glass Beads. Soil Sci. Soc. Amer. Proc., Vol. 27, No. 1, 10-13.

34. Olmstead, L. B., L. T. Alexander and H. E. Middleton. 1930. A Pipette Method of Mechanical Analysis of Soils Based on Improved Dispersion Procedure. USDA Tech. Bul. No. 170.

35. Olsen, S. R. and W. D. Kemper. 1968. Movement of Nutrients to Plant Roots. Advances in Agronomy, Vol. 20, 91-151.

36. Orlob, G. T. and G. N. Radhakrishna. 1958. The Effects of Entrapped Gasses on the Hydraulic Characteristics of Porous Media. Trans. Amer. Geophys. Union, Vol. 39, No. 4, 648-659.

37. Porter, L. K., W. D. Kemper, R. D. Jackson and B. A. Stewart. 1960. Chloride Diffusion in Soil as Influenced by Moisture Content. Soil Sci. Soc. Amer. Proc., Vol. 24, No. 6, 460-463.

38. Rose, D. A. and J. B. Passioura. 1971. Analysis of Experiments on Hydrodynamic Dispersion. Soil Science, Vol. 111, No. 4, 252-257.

39. Rose, D. A. and J. B. Passioura. 1971. Gravity Segregation During Miscible Displacement Experiments. Soil Science, Vol. 111, No. 4, 253-265.

40. Scheideidegger, A. E. 1957. On the Theory of Flow of Miscible Phases in Porous Media. Compt. rend. Ass. Gen. Toronto, Assoc. Intern. Hydrol. Scient., 2, 236-242.

41. Stewart, G. L. 1971. The Behavior of Tritium in the Soil. Tritium Messenger Graphics, Las Vegas, Nevada, 462-470.

42. Stewart, G. L. 1972. Clay-Water Interaction, the Behavior of $3_H$ and $2_H$ in Adsorbed Water, and the Isotope Effect. Soil Sci. Soc. Amer. Proc., Vol. 36, No. 3, 421-426.

43. Slichter, C. S. 1905. Field Measurement of Rate of Movement of Underground Water. USGS Water Supply Paper 140, 85 pp.

44. Thomas, G. W. and A. R. Swoboda. 1970. Anion Exclusion Effects on Chloride Movement in Soils. Soil Science, Vol. 10, No. 3, 163-166.

45. Turner, G. S. 1957. Flow Structure in Packed Beds. Chemical Engineering Science, Vol. 7, 156-165.